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Novel Developments in Organonitrogen Fluorine Chemistry from Carbon-Nitrogen Multiple Bonds

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Darryl D. DesMarteau

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The synthesis, reactions and selected structures of a variety of fluoroorganic compounds of nitrogen were studied. All of the chemistry is based on the reactivity of carbon-nitrogen double and triple bonds with a few examples of analogous sulfur-nitrogen systems. The chemistry is based predominantly on the reactivity of these unsaturated systems with nucleophiles (fluoride ion mainly) and with oxidizing agents (halogens and peroxides).

Fluoride ion from MX (M=K, Rb, Cs) attacks nitriles to form $R_xCF=N^-$ anions which are easily oxidized by the halogens F_2, Cl_2 and Br_2 to the respective $R_xCF=NX$. The resultant imine can be further attacked by fluoride ion forming $R_xCF_2NX^-$ which can be further ionized to $R_xCF_2NX_2$. in certain cases if $R_x=F$ and $X=F$, the alkamine anion is also a reactive nucleophile and nuclephilic substitution reactions lead to a variety of novel compounds. Of special interest are the diaziridines

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$CF_3N - CF_2$ (X=F, Cl, Br, CF3) formed in this way.

$$\begin{array}{c} CF_3N - CF_2 \\ \backslash \; N \; / \\ | \\ X \end{array}$$

Other nitriles such as FC≡N lead to simple new molecules such as CF_2=NBr, which completed the series CF_2=NX (X=F, Cl, Br). These simple 5-atom molecules are now well characterized structurally and theoretically and their chemistry is fascinating. Still other nitriles such as $(CN)_2$ & CNCF=NF provided an opportunity to compare the reactivity of both -C≡N and $\begin{array}{c} \backslash \\ C=N - \\ / \end{array}$ bonds towards fluoride ion in the same molecule. Remarkably, of the 49 structural isomers possible in $X_2NCF_2CF_2NX_2$, XN=CFCF=NX, XN=CFCF$_2$NX$_2$, NCCF$_2$-NX$_2$ and NCCF=NX for combinations of X=F, Cl, Br, at least 24 isomers have now been positively identified.

In the sulfur analogs, FS≡N and F_3S≡N lead to related novel compounds, although the chemistry is more limited. The (fluoroimido)tetrafluorosulfur, SF_4=NF provided a wealth of interesting chemistry including the first example of magnetic non-equivalence in an octahedral system induced by a chiral center in cis-FSO$_2$OSF$_4$N*FX (X=Cl, Br, OSO$_2$F).

Throughout this work, reactivity of N-halogens (Br, Cl) were utilized to advantage to prepare novel compounds. Reactions of CF_2=NCl with perhaloalkenes gave routes to new imines CF_2=NR$_x$. These were oxidized to new examples of oxaziridines $\begin{array}{c} R_xN - CF_2 \\ \backslash \; / \\ O \end{array}$ by CF$_3$OOH. Thermal addition of R$_x$CF=NBr to perhaloalkenes provided routes to novel perhaloheterodienes of the type

$$\begin{array}{c} O \\ \| \\ R_xC\text{-}N=CFCF_2X \end{array} \text{ and } R_xCCl=NCCl=CF_2X.$$

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4.   Some Reactions of (Fluoroimido)tetrafluorosulfur
5.   Novel Ammonium Hexafluoroarsenate Salts From Reactions of $(CF_3)_2NH$, $CF_3N(OCF_3)H$, CF_3NHF and SF_5NHF With the Strong Acid HF/AsF_5.
6.   An Efficient Syntheses of N-Bromoperhalo-1-alkanimines.
7.   Synthesis of CF_3NBr_2 and CF_3NBrCl. Novel Metal Fluoride Promoted Conversion of N-Cl Bonds to N-Br Bonds.
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19.   Cesium Fluoride Promoted Halogenation of Cyanogen by Chlorine and Bromine and Selected Reactions of Products.
20.   Halogen Exchange Reactions of Perhalo-3-Azoalkenes and Their Subsequent Dehalogenation to Form Hetero-1,3-dienes.
21.   An Improved Synthesis of Dichlorofluoroamine, $FNCl_2$.
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Research Accomplished

The research carried out under this grant is summarized in the following 22 publications, copies of which are contained in the appendix. These are arranged chronologically. The goal of this research was to utilize the reactivity of carbon-nitrogen multiple bonds towards nucleophiles and oxidizing agents to prepare novel perfluoroorganonitrogen compounds. More than 130 new compounds were prepared and characterized. Detailed structural and theoretical studies were carried out on $CF_2=NX$ (X=F, Cl, Br, $N=CF_2$). The diversity and fascinating properties of highly fluorinated compounds should be evident. The future in this as yet young area of chemistry, is clearly one of great potential.

1983

1. Synthesis of 1,1-Difluoro-2-azaperhalo-1-butenes and Their Conversion of Oxaziridines.

1984

2. Some Novel Reactions of N-Chlorodifluoromethanimine

3. N-Bromodifluoromethanimine

4. Some Reactions of (Fluoroimido)tetrafluorosulfur

5. Novel Ammonium Hexafluoroarsenate Salts From Reactions of $(CF_3)_2NH$, $CF_3N(OCF_3)H$, CF_3NHF and SF_5NHF With the Strong Acid HF/AsF_5.

6. An Efficient Syntheses of N-Bromoperhalo-1-alkanimines.

7. Synthesis of CF_3NBr_2 and CF_3NBrCl. Novel Metal Fluoride Promoted Conversion of N-Cl Bonds to N-Br Bonds.

1985

8. (Perfluoroalkylimino)selenyl Chlorides

1986

9. Some Reactions of Highly Halogenated N-Bromo-1-fluoro-1-alkanimines.

10. Cycloaddition and Oxygen-Transfer Reactions of 2-(Trifluoromethyl)-3,3-difluorooxaziridine.

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15. Microwave Spectrum Quadrupole Coupling Constants, and Structure of N-Bromodifluoromethanimine.

16. Molecular Structure and Internal Rotation Potential of Perhalo-2,3-diaza-1,3-butadiene, $CF_2=N-N=CF_2$. An Electron Diffraction and ab Initio Study.

1990

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18. Cesium Fluoride-Assisted Reactions of Syn and Anti N-Fluoro-1-Cyano-1-Fluoromethanimine With Chlorine and Bromine.

1991

19. Cesium Fluoride Promoted Halogenation of Cyanogen by Chlorine and Bromine and Selected Reactions of Products.

20. Halogen Exchange Reactions of Perhalo-3-Azoalkenes and Their Subsequent Dehalogenation to Form Hetero-1,3-dienes.

21. An Improved Synthesis of Dichlorofluoroamine, $FNCl_2$.

22. Synthesis of Novel Perhalo 1,3-Heterodienes from N-Bromoperhalo-1-alkanimines.

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8. Dr. Anthony Wade, UK, postdoctoral.
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APPENDIX

PUBLICATION

REPRINTS

Synthesis of 1,1-Difluoro-2-azaperhalo-1-butenes and Their Conversion to Oxaziridines[1]
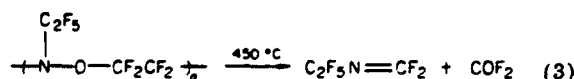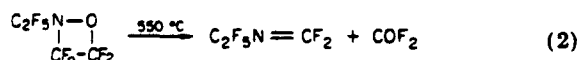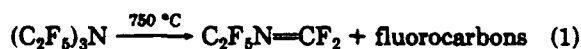
Yuan Y. Zheng[2] and Darryl D. DesMarteau*

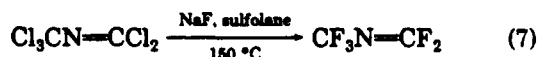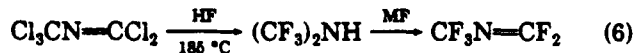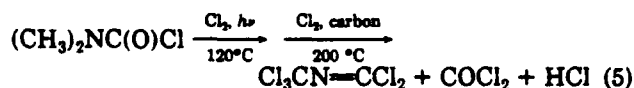*Department of Chemistry, Clemson University, Clemson, South Carolina 29631*

Received June 14, 1983

At elevated temperatures, N-chlorodifluoromethanimine (CF_2=NCl) adds to perhaloalkenes of the type CF_2=CFX, forming CF_2=NCF$_2$CFXCl (X = F, Cl, Br) in good yields. Reaction of these butenes with trifluoromethyl hydroperoxide (CF_3OOH) gives $CF_3OOCF_2NHCF_2CFXCl$, and subsequent treatment with KHF_2 forms the corresponding oxaziridine, $\overline{OCF_2NCF_2}CFXCl$, in excellent yield. Eight new compounds, along with the previously reported CF_2=NCF$_2$CF$_2$Cl, were characterized by their IR, NMR, and mass spectra and physical properties.
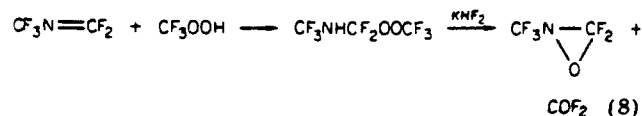
The synthesis of 1,1-difluoro-2-azaperhalo-1-alkenes or N-(perhaloalkyl)difluoromethanimines of the type CF_2=NR$_x$ is very difficult, and only a few such compounds are known. Examples have, in general, been prepared by pyrolysis of perfluoro tertiary amines and by the pyrolysis of perfluoro-2-alkyl-1,2-oxazetidines or the corresponding copolymer formed from R$_f$NO and CF_2=CF$_2$[3] (eq 1–3). In the case of perfluoro-2-azapropene, more practical methods of synthesis have been developed by utilizing $(CF_3)_2NC(O)F$, available from electrochemical fluorination of $(CH_3)_2NC(O)F$,[4] or Cl_3CN=CCl$_2$ from high-temperature chlorination of $(CH_3)_2NC(O)Cl$[5] (eq 4–7).

$$(C_2F_5)_3N \xrightarrow{750\ ^\circ C} C_2F_5N\text{=}CF_2 + \text{fluorocarbons} \quad (1)$$

$$\underset{\underset{CF_2-CF_2}{|\quad\ |}}{C_2F_5N-O} \xrightarrow{550\ ^\circ C} C_2F_5N=CF_2 + COF_2 \quad (2)$$

$$\underset{\underset{}{|}}{\overset{\overset{C_2F_5}{|}}{+N-O-CF_2CF_2+_n}} \xrightarrow{450\ ^\circ C} C_2F_5N=CF_2 + COF_2 \quad (3)$$

$$(CF_3)_2NC(O)F \xrightarrow{575\ ^\circ C} CF_3N\text{=}CF_2 + COF_2 \quad (4)$$

$$(CH_3)_2NC(O)Cl \xrightarrow[120\ ^\circ C]{Cl_2,\ h\nu} \xrightarrow[200\ ^\circ C]{Cl_2,\ carbon}$$
$$Cl_3CN\text{=}CCl_2 + COCl_2 + HCl \quad (5)$$

$$Cl_3CN\text{=}CCl_2 \xrightarrow[185\ ^\circ C]{HF} (CF_3)_2NH \xrightarrow{MF} CF_3N\text{=}CF_2 \quad (6)$$

$$Cl_3CN\text{=}CCl_2 \xrightarrow[150\ ^\circ C]{NaF,\ sulfolane} CF_3N\text{=}CF_2 \quad (7)$$

Our interest in perhalogenated azaalkenes relates in part to the fascinating chemistry of $\overline{CF_3NCF_2O}$,[6] which is prepared from CF_3N=CF$_2$[7] (eq 8). Extension of this

$$CF_3N\text{=}CF_2 + CF_3OOH \longrightarrow CF_3NHCF_2OOCF_3 \xrightarrow{KHF_2} CF_3N\overset{\diagdown\diagup}{\underset{O}{-}}CF_2 +$$
$$COF_2 \quad (8)$$

reaction sequence to SF_5N=CF$_2$[8] suggested that a variety

of R_xN=CF$_2$ azaalkenes might similarly lead to new oxaziridines. A patent on the use of CF_2=NCl for the direct synthesis of CF_2=NR$_x$ compounds by thermal addition to olefins appeared to be a particularly promising route to new azaalkenes.[9] In this paper we present details for the synthesis of CF_2=NCF$_2$CFXCl (X = F, Cl, Br) via the addition of CF_2=NCl to CF_2=CFX. These azaalkenes are converted to the corresponding oxaziridines ClXCFCF$_2$-$\overline{NCF_2O}$ in excellent yields via the intermediate amines $ClXCFCF_2NHCF_2OOCF_3$ formed by addition of CF_3OOH.

Experimental Section

General Methods. All work was carried out in Pyrex or stainless steel (Types 304 and 316) vacuum systems equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements. Temperatures were measured by using a digital-indicating iron–constantan thermocouple.

Infrared spectra were taken on a Perkin-Elmer 337, 1330, 180, or 1430 spectrometer. A 10-cm glass cell fitted with AgCl or KCl windows was employed. NMR spectra were recorded on a Varian XL-100-15 spectrometer by using 80 mol % CFCl$_3$ as a solvent and an internal reference or on a JEOL FX-90Q spectrometer by using ~68 mol % CCl$_4$ as the solvent, ~30 mol % CDCl$_3$ as an internal lock, and ~1 mol % CFCl$_3$ as an internal reference. Proton chemical shifts were measured against external Me$_4$Si and are given in δ units (with the coupling constants given in hertz). Mass spectra were taken on a Finnigan 4021-C or a Hewlett-Packard 5985B instrument at 70 eV for electron-impact (EI) and chemical-ionization [CI (CH$_4$)] spectra. Samples were introduced by direct gas injection.

Melting points were determined by a modified Stock procedure. Vapor pressures as a function of temperature were determined by using a small isoteniscope.[10] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purification of reaction products, GLC was carried out on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. Columns of 10, 2, or 1 ft × $^3/_8$ in. packed with 35% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P were used.

Reagents. The olefins CF_2=CFX (X = F, Cl, Br) were obtained from PCR, Inc., and Cl$_2$, F$_2$, KHF$_2$, and ClCN were obtained from commercial sources and appropriately purified before use. ClF was prepared by reaction of equimolar amounts of Cl$_2$ and F$_2$ in a Monel bomb at 250 °C. CF_3OOH was prepared by the liturature method.[11] CF_2=NCl was prepared by a modification of the literature method.[12]

(1) Work carried out in part at Kansas State University, Manhattan, KS 66506.

(2) Visiting Scholar, People's Republic of China.

(3) For a review of known compounds see: Haas, A. "Gemelin Handbook of Inorganic Chemistry"; Springer-Verlag: New York, 1981; Part 9, p 125.

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(6) Lam, W. Y.; DesMarteau, D. D. *J. Am. Chem. Soc.* 1982, 104, 4034.

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(8) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* 1980, 19, 1330.

(9) Young, D. E.; Anderson, L. R.; Fox. W. B. U.S. Patent 3689563; *Chem. Abstr.* 1972, 78, 29213t.

(10) Smith, A.; Menzies, A. W. C. *J. Am. Chem. Soc.* 1910, 32, 897.

(11) Bernstein, P. A.; Hohorst, F. A.; DesMarteau, D. D. *J. Am. Chem. Soc.* 1971, 93, 3882.

To a 150-mL stainless steel reactor at −196 °C was added 30 mmol of ClCN by vacuum transfer, followed by 60 mmol of ClF. The mixture was then allowed to warm slowly to 22 °C in a cold dewar container initially at −196 °C. After being allowed to stand at 22 °C for 20 h, the contents of the cylinder were separated through a −78 °C trap to collect ClCF$_2$NCl$_2$ (∼85%). A 10-mmol sample of ClCF$_2$NCl$_2$ was then heated in a 100-mL Pyrex vessel for 5 h at 135 °C. The contents were then transferred onto 10 g of Hg and allowed to stand for 20 min at 22 °C. The volatiles were then separated through traps at −95, −125, and −196 °C. Pure CF$_2$=NCl (85%) collected in the −125 °C trap.

Reactions of CF$_2$=NCl with Olefins. Reactions were carried out in a 66-mL glass reaction vessel fitted with a glass−Teflon valve. In a typical reaction, CF$_2$=NCl (8 mmol) and olefin (4–8 mmol) were condensed into the flask, and it was then heated for 8–12 h at 150–200 °C. The products were separated by pumping through traps held at appropriate temperatures. Pure samples of the perhalo-2-aza-1-butenes were obtained by reseparating the crude products by using trap-to-trap distillation or by GLC on a 10 ft × $^3/_8$ in. stainless steel column.

CF$_2$=NCF$_2$CF$_2$Cl: yield 40%; bp 31.9 °C; mol wt 198.0, calcd 199.5; log P (torr) = 7.489 − (1405.9/T); ΔH$_{vap}$ = 6.43 kcal/mol; ΔS$_{vap}$ = 21.1 eu; IR 1791 (s), 1740 (w), 1312 (s), 1288 (s), 1250 (s), 1204 (s), 1163 (s), 1113 (s), 999 (s), 916 (s), 819 (w), 779 (w), 714 (w) cm^{-1}; MS (CI, major), m/z 200/202 [(MH)$^+$], 180/182 [(M − F)$^+$]; MS (EI), m/z 164 [(M − Cl)$^+$], 114 [(C$_2$F$_4$N)$^+$], 85/87 [(CF$_2$Cl)$^+$]; ^{19}F NMR (F^{A}F^{B}C=NCF$_2^C$CF$_2^D$Cl) A = −45.3 (br d), B = −29.3 (br d), C = −95.0 (m), D = −73.9 (m), J$_{AB}$ = 83, J$_{AC}$ = J$_{BC}$ = 10.0, J$_{AD}$ ≃ J$_{BD}$ = 2.0, J$_{CD}$ = 4.0.

CF$_2$=NCF$_2$CFCl$_2$: yield, 48%; bp 64.9 °C; mol wt 214.0, calcd 215.95; log P (torr) = 7.828 − (1672.5/T); ΔH$_{vap}$ = 7.65 kcal/mol; ΔS$_{vap}$ = 22.6 eu; IR 1795 (s), 1741 (m), 1413 (w), 1312 (s), 1251 (s), 1204 (s), 1163 (s), 1107 (s), 1040 (m), 981 (m), 899 (s), 858 (s), 810 (s), 705 (w), 649 (w), 628 (w) cm^{-1}; MS (CI, major) m/z 216/218/220 [(MH)$^+$], 196/198/200 [(M − F)$^+$], 180/182 [(M − Cl)$^+$]; MS (EI), m/z 180/182 [(M − Cl)$^+$], 151/153/155 [(C$_2$F$_3$Cl$_2$)$^+$], 114 [(C$_2$F$_4$N)$^+$], 101/103/105 [(CFCl$_2$)$^+$]; ^{19}F NMR (F^{A}F^{B}C=NCF$_2^C$CF^{D}Cl$_2$) A = −45.5 (br d), B = −29.1 (br d), C = −92.3 (m), D = −75.7 (tt), J$_{AB}$ = 82, J$_{CD}$ = 9.0, J$_{AC}$ or J$_{BC}$ = 11.5, J$_{AB}$ or J$_{BC}$ = 9.0, J$_{AD}$ ≃ J$_{BD}$ = 3.0.

CF$_2$=NCF$_2$CFBrCl: yield 30%; bp 84.9 °C; mol wt 257.0, calcd 260.4; log P (torr) = 7.642 − (1704.8/T); ΔH$_{vap}$ = 7.80 kcal/mol; ΔS$_{vap}$ = 21.8 eu; IR 1785 (s), 1779 (s), 1573 (w), 1415 (w), 1305 (s), 1247 (s), 1199 (s), 1154 (s), 1100 (s), 1026 (m), 993 (m), 973 (m), 887 (s), 859 (s), 768 (s), 729 (m), 601 (w) cm^{-1}; MS (CI, major), m/z 260/262/264 [(MH)$^+$], 240/242/244 [(M − F)$^+$], 224/226 [(M − Cl)$^+$], 195/197/199 [(C$_2$F$_3$BrCl)$^+$], 116/118 [(C$_2$F$_3$Cl)$^+$]; MS (EI), m/z 180/182 [(M − Br)$^+$], 114 [(C$_2$F$_4$N)$^+$]; ^{19}F NMR (F^{A}F^{B}C=NCF$_2^C$CF^{D}BrCl) A = −45.6 (br d), B = −31.1 (br d), C = −90.9 (m), D = −75.1 (tt), J$_{AB}$ = 89, J$_{AC}$ = J$_{BC}$ = J$_{CD}$ = 11.0, J$_{AD}$ = J$_{BD}$ = 2.5.

Reactions of CF$_2$=NCF$_2$CFXCl with CF$_3$OOH. Reactions were carried out in a 100-mL glass bulb fitted with a glass−Teflon valve. In a typical reaction, the CF$_2$=NCF$_2$CFXCl (3.0 mmol) and CF$_3$OOH (4.0 mmol) were condensed into the glass bulb at −196 °C. The vessel was then allowed to stand in an ice bath for 1 day. The reaction mixture was separated by pumping through traps at −50, −78, and −196 °C. Both the −78 and −196 °C traps contained some unreacted starting materials (CF$_3$OOH and CF$_2$=NCF$_2$CFXCl). Essentially pure CF$_3$OOCF$_2$NHCF$_2$CFXCl was obtained by refractionation of the contents of the −50 °C trap by using the same procedure.

CF$_3$OOCF$_2$NHCF$_2$CF$_2$Cl: yield 76%; mol wt 300.1; calcd 301.5; IR 3455 (m), 1892 (w), 1774 (w), 1613 (w), 1510 (s), 1502 (s), 1424 (vw), 1327 (s), 1283 (s), 1095 (s), 1025 (vw), 972 (s), 875 (s), 837 (s), 793 (vw), 768 (vw), 740 (m), 718 (m), 669 (w), 646 (m), 633 (m) cm^{-1}; MS (CI, major), m/z 302/304 [(MH)$^+$], 282/284 [(M − F)$^+$], 266 [(M − Cl)$^+$], 180/182 [(C$_3$F$_5$NCl)$^+$], 160/162 [(C$_3$F$_4$NCl)$^+$], 64 [(CF$_2$N)$^+$]; ^{19}F NMR (CF$_3^A$OOCF$_2^B$N(H)-CF$_2^C$CF$_2^D$Cl) A = −68.6 (t), B = −68.0(m), C = −93.4 (qt), D = −73.6 (m), ^{1}H NMR δ$_H$ = 5.0 (br s), J$_{AB}$ = 4.0, J$_{BH}$ = 4.0, J$_{BC}$ = 9.4, J$_{BD}$ = 1.4, J$_{CH}$ = 9.4, J$_{CD}$ = 3.0, J$_{DH}$ ≃ 0.

CF$_3$OOCF$_2$NHCF$_2$CFCl$_2$: yield 75%; mol wt 317.0, calcd 318.0; IR 3445 (m), 1493 (s), 1313 (s), 1273 (s), 1228 (s), 1208 (s), 1119 (s), 1095 (s), 904 (s), 815 (w), 710 (w), 610 (w) cm^{-1}; MS (CI, major), m/z 298/300/302 [(M − F)$^+$], 216/218/220 [(C$_3$F$_5$NCl$_2$H)$^+$], 196/198/200 [(C$_3$F$_4$NCl$_2$)$^+$], 180/182 [(C$_3$F$_5$NCl)$^+$], 136 [(C$_3$F$_4$N)$^+$]; ^{19}F NMR (CF$_3^A$OOCF$_2^B$N(H)-CF$_2^C$CF^{D}Cl$_2$) A = −68.5 (t), B = −68.0 (m), C = −91.1 (m), D = −74.8 (t), ^{1}H NMR δ$_H$ = 5.0 (br s), J$_{AB}$ = J$_{BH}$ = 3.7, J$_{BC}$ = J$_{CH}$ = 9.4, J$_{CD}$ = 8.0, J$_{DH}$ = J$_{BD}$ = 1.0.

CF$_3$OOCF$_2$NHCF$_2$CFBrCl: yield 86%; mol wt 368.8, calcd 362.4; IR 3441 (m), 1495 (s), 1418 (w), 1308 (s), 1278 (vs), 1235 (vs), 1206 (vs), 1122 (vs), 1114 (vs), 1014 (w), 861 (s), 808 (m), 772 (w), 731 (m), 615 (w) cm^{-1}; MS (CI, major), m/z 200–400, 362/364/366 [(MH)$^+$], 342/344/346 [(M − F)$^+$], 260/262/264 [(C$_3$F$_5$NBrCl)$^+$], 240/242/244 [(C$_3$F$_4$NBrCl)$^+$]; ^{19}F NMR (CF$_3^A$OOCF$_2^B$NHCF$_2^C$CF^{D}BrCl) A = −68.5 (t), B = −68.0 (m), C = −90.0 (m), D = −74.1 (m), ^{1}H NMR δ$_H$ = 5.0 (br s), J$_{AB}$ ≃ J$_{BH}$ = 4.3, J$_{BC}$ = J$_{CH}$ = J$_{CD}$ = 10.3, J$_{BH}$ ≃ J$_{BD}$ ≃ 1.0.

Reactions of CF$_3$OOCF$_2$NHCF$_2$CFXCl with KHF$_2$. Reactions were carried out in a 75-mL stainless steel reactor. In a typical reaction, dried KHF$_2$ (∼10 g) was placed in the reactor in a drybox. The vessel was then evacuated and cooled to −196 °C, and CF$_3$OOCF$_2$NHCF$_2$CFXCl was added by vacuum transfer. The reactor was allowed to stand for 1 day at 22 °C, and the volatile products were then distilled through a series of cold traps, giving COF$_2$ and ClXCFCF$_2$NCF$_2$O as the major products. Pure samples of the oxaziridines were obtained by GLC.

ClCF$_2$CF$_2$NCF$_2$O: yield 70%; bp 37.2 °C; mol wt 214.1, calcd 215.5; log P (torr) = 7.5081 − (1436.17/T); ΔH$_{vap}$ = 6.57 kcal/mol; ΔS$_{vap}$ = 21.2 eu; IR 1437 (s), 1316 (m), 1272 (s), 1249 (s), 1176 (s), 1118 (s), 1063 (m), 980 (s), 892 (m), 850 (m), 780 (m), 694 (w), 662 (w), 640 (w), 602 (m), 557 (w), 537 (w), 472 (w) cm^{-1}; MS (CI, major), m/z 150–300, 216/218 [(MH)$^+$], 200/202 [(MH − O)$^+$], 178/180 [(C$_3$F$_4$ClNOH)$^+$], 180/182 [(C$_3$F$_5$NCl)$^+$], 158/160 [(C$_3$F$_3$ClNO)$^+$], 150/152 [(C$_2$F$_4$ClNH)$^+$]; ^{19}F NMR (ClCF^{A}F^{B}CF^{C}F^{D}NCF^{E}F^{F}O; approximate values for C, D, and E taken from computer simulation; see discussion) A ≃ B = −71.8 (m), C = −109.4 (m), D = −104.1 (m), E = −105.2 (m), F = −89.5(m); J$_{AB}$ ≃ 1.0, J$_{AC}$ ≃ J$_{AD}$ ≃ 5.0, J$_{AE}$ ≃ J$_{AF}$ ≃ 0, J$_{BC}$ = J$_{BD}$ = 5.0, J$_{BE}$ ≃ J$_{BF}$ ≃ 0, J$_{CD}$ = 190, J$_{CE}$ = 40, J$_{CF}$ ≃ J$_{DF}$ ≃ 8.0, J$_{DE}$ = 20, J$_{EF}$ = 2.0.

Cl$_2$CFCF$_2$NCF$_2$O: yield 85%; bp 70.5 °C; mol wt 229.0, calcd 231.94; log P (torr) = 7.7775 − (1682.65/T); ΔH$_{vap}$ = 7.69 kcal/mol; ΔS$_{vap}$ = 22.4 eu; IR 1423(s), 1265 (s), 1159 (s), 1088 (s), 1061 (s), 1025 (m), 950 (m), 895 (s), 834 (s), 767 (s), 694 (m), 650 (m), 522 (w) cm^{-1}; MS, (CI, major), m/z 150–300, 232/234/236 [(MH)$^+$], 216/218/220 [(MH − O)$^+$], 212/214/216 (?), 196/198 [(M − Cl)$^+$], 194/196/198 [(MH − F$_2$)$^+$], 174/176/178 [(C$_3$F$_2$Cl$_2$NO)$^+$], 178/180/182 [(C$_3$F$_5$Cl$_2$NH)$^+$], 166/168/170 [(C$_2$F$_3$Cl$_2$NH)$^+$], 158/160 [(C$_3$F$_3$ClNO)$^+$], 150/152 [(C$_2$F$_4$ClN)$^+$]; ^{19}F NMR (Cl$_2$CF^{A}CF^{B}F^{C}NCF^{D}F^{E}O; approximate values for B, C, and D taken from computer simulation) A = −89.2 (t), B = −106.6 (m), C = −100.3 (m), D = 104.7 (m), E = −74.2 (td), J$_{AB}$ = J$_{AC}$ = 6.0, J$_{AD}$ = J$_{AE}$ ≃ 0, J$_{BC}$ = 190, J$_{BD}$ = 33, J$_{BE}$ = J$_{CE}$ = 8.0, J$_{CD}$ = 22.0, J$_{DE}$ = 3.0.

ClBrCFCF$_2$NCF$_2$O: yield 93%; bp 90.4 °C; mol wt 275.1, calcd 276.40; log P (torr) = 7.4681 − (1667.85/T); ΔH$_{vap}$ = 7.63 kcal/mol; ΔS$_{vap}$ = 20.9 eu; IR 1434 (s), 1271 (s), 1235 (m), 1193 (m), 1163 (m), 1096 (m), 1064 (m), 1024 (m), 948 (w), 864 (m), 834 (m), 812 (m), 764 (m), 693 (w), 646 (w) cm^{-1}; MS (CI, major), m/z 150–300, 276/278/280 [(MH)$^+$ weak], 260/262/264 [(MH − O)$^+$], 238/240/242 [(MH − F$_2$)$^+$], 218/220/222 [(C$_3$F$_2$BrClNO)$^+$], 202/204 [(C$_3$F$_3$BrNO)$^+$], 158/160 [(C$_3$F$_3$ClNO)$^+$]; ^{19}F NMR (ClBrCF^{A}CF^{B}F^{C}NCF^{D}F^{E}O; mixture of diastereoisomers, approximate values of chemical shifts and coupling constants given by comparison with previous oxaziridine) A = −89 (m), B = −105 (m), C = −98 (m), D = −104 (m), E = −74 (m), J$_{BC}$ = 200, J$_{BD}$ = 40, J$_{CD}$ = 30, and other coupling constants similar to Cl$_2$CFCF$_2$NCF$_2$O but not easily determined (see discussion).

Results and Discussion

2-Azaperhalo-1-butenes. The thermal addition of

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(12) Young, D. E.; Anderson, L. R.; Fox, W. B. *J. Chem. Soc., Chem. Commun.* 1970, 395.

CF_2=NCl to the olefins CF_2=CFX (X = F, Cl, Br) proceeds readily in the temperature range 150–200 °C (eq 9).

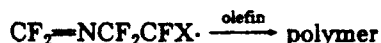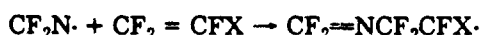$$CF_2=NCl + CF_2=CFX \rightarrow CF_2=NCF_2CFXCl \quad (9)$$
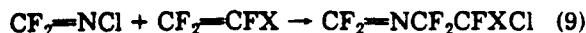
The yields of addition product depend on many factors including pressure, reaction time, temperature, stoichiometry, and the type of reaction vessel. The earlier report of a 75% yield for this reaction with CF_2=CF$_2$ in a 30-mL stainless steel vessel at 150 °C, employing a 1:1 stoichiometry, 4 h reaction time, and total initial pressure of ~11 atm,[9] gave only very low yields of the addition product in our hands. The major products were polymeric. We ultimately found that a Pyrex reaction vessel was more suitable. By trial and error, we found that a 2:1 ratio of imine to olefin, a temperature of 150 °C, an initial pressure of ~7 atm and a reaction time of 10 h gave acceptable yields with CF_2=CFX.

The conversion based on the amount of CF_2=NCl consumed is 75–95%, but the yield of CF_2=NCF$_2$CFXCl based on starting olefin is typically only 20–50%. The high recovery of unreacted CF_2=NCl combined with the complete disappearance of the olefin, shows that a major side reaction involves the formation of oligomers, telomers, and higher molecular weight polymers of the olefin. These polymers have not been identified except for CF_2=N-$(CF_2CFX)_2Cl$, which was identified by mass spectrometry. In all reactions, after removal of unreacted CF_2=NCl and the adduct CF_2=NCF$_2$CFXCl, a low volatile residue remained in the reactor. This residue varied in appearance from a viscous oil to a gel, to a solid, or to a combination of these. In general, these residues were soluble in acetone.

Attempts to extend the reaction of CF_2=NCl to hydrogen-containing olefins were not very successful. With CF_2=CH$_2$ and CH$_2$=CH$_2$, reaction under similar conditions gave a plethora of products including HCl and SiF$_4$ (from HF). Small amounts of CF_2=NCF$_2$CH$_2$Cl were apparently formed with CF_2=CH$_2$, but no evidence for CF_2=NCH$_2$CH$_2$Cl was found. In both cases the major products were polymeric, and these reactions were abandoned.

The addition of CF_2=NCl to CF_2=CFX is regiospecific and is probably a free-radical process as illustrated in Scheme I. The chain-transfer reaction leading to the

Scheme I

$$CF_2 = NCl \rightleftharpoons CF_2N\cdot + Cl\cdot$$

$$CF_2N\cdot + CF_2 = CFX \rightarrow CF_2=NCF_2CFX\cdot$$

$$CF_2=NCF_2CFX\cdot \xrightarrow{\text{olefin}} \text{polymer}$$

$$CF_2=NCF_2CFX\cdot + CF_2=NCl \rightarrow CF_2=NCF_2CFXCl + CF_2N\cdot$$

2-azaperhalo-1-butene clearly competes effectively with other processes. The polymers formed, while not characterized, are potentially very interesting because they could be readily converted to isocyanates and other products if they contain terminal CF_2=N groups.

The identification of CF_2=NCF$_2$CFXCl is straightforward based on the data given in the Experimental Section. Molecular ions are observed for each compound in the CI mass spectra, and each contains a strong absorption in the IR near 1800 cm^{-1} due to ν(C=N).[13] The ^{19}F NMR exhibit the expected AB pattern for the CF_2=N group with J_{AB} near 85 Hz.[14] Assuming $^4J_{FF}$ to be larger than $^5J_{FF}$, the

structural isomers are readily assigned for X = Cl and Br. Similar conclusions may be made from the chemical shift of the N–CF$_2$ group. For the alternative structural isomer CF_2=NCFXCF$_2$Cl, the chemical shift of the CF$_2$Cl group would be expected at considerably higher field than observed.[15]

Reaction of CF_2=NCF$_2$CFXCl with CF$_3$OOH. The previously observed addition of CF$_3$OOH to CF_2=NCF$_3$[7] and CF_2=NSF$_5$[8] proceeds readily with CF_2=NCF$_2$CFXCl under similar conditions (eq 10). The expected amines

$$CF_2=NCF_2CFXCl + CF_3OOH \rightarrow$$
$$CF_3OOCF_2N(H)CF_2CFXCl \quad (10)$$
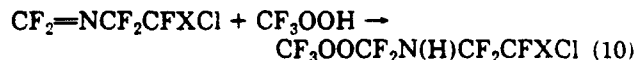
are isolated in very good yield. However, this is not a general reaction with all fluorinated imines; CF$_3$OOH will not add to CF_2=NF, CF_2=NCl, NCCF=NF, or $(CF_3)_2$N-CF=NCF$_3$ under the same conditions. The addition of CF$_3$OOH to CF_2=NCF$_2$CFXCl proceeds mainly in the condensed phase. It was previously found with CF_2=N-CF$_3$ that the yields increased for a given reaction scale as the reactor volume decreased. In this work the rate of reaction of CF_2=NCF$_2$CFXCl under identical conditions was the slowest for X = F. We attribute this to the lower boiling point of CF_2=NCF$_2$CF$_2$Cl, resulting in a larger fraction of the compound initially present in the gas phase. Consistent with this, the 0 °C reaction temperature also gave higher yields than reactions carried out at 22 °C. In addition, at 22 °C, some O$_2$ is formed from the decomposition of CF$_3$OOH.[16] This results in the formation of HF, which rapidly adds to CF_2=NCF$_2$CFXCl to form CF$_3$NHCF$_2$CFXCl as a significant byproduct.[17]

The pure CF$_3$OOCF$_2$NHCF$_2$CFXCl amines are apparently stable in glass at 22 °C. No detectable decomposition was observed in routine handling of the compounds in the vacuum system. The characterization of the compounds is given in the Experimental Section. Parent MH$^+$ molecular ions are observed in the CI mass spectrum for X = F and Br, and (M – F)$^+$ is observed for X = Cl. The IR and NMR spectra are consistent with that of CF$_3$OOCF$_2$NHCF$_3$,[7] and the extensive J_{F-F} and J_{H-F} couplings strongly support the structural formula indicated. Additional proof of the peroxide linkage is given by the fact that the compounds are strongly oxidizing toward aqueous KI.

Reaction of CF$_3$OOCF$_2$NHCF$_2$CFXCl with KHF$_2$. The conversion of CF$_3$OOCF$_2$NHCF$_3$ to the novel oxaziridine CF$_3$N̄CF$_2$O was first accomplished by reaction of CF$_3$OOCF$_2$NHCF$_3$ with NaF.[7] Subsequently, a more detailed study of this reaction with a variety of metal fluorides indicated that the metal fluoride had to be effective in complexing HF and that the resultant oxaziridine was very easily isomerized by active fluorides to CF$_3$NF-C(O)F.[18] For alkali metal fluorides which complex HF, the order of reactivity for ring opening and isomerization was NaF < KF < CsF. However, even NaF gave a significant yield of CF$_3$NFC(O)F in the preparation of the oxaziridine. Potassium bifluoride, on the other hand, is effective in complexing HF but is of low fluoride ion ac-

(13) In CF_2=NX (X = Cl, F) ν (C=N) is at 1728 and 1740 cm^{-1}, respectively. Christen, D.; Oberhammer, H.; Hammaker, R. M.; Chang, S. C.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 6186.

(14) These J_{AB} values in CF_2=NX (X = Cl, F) are 69.0 and 52.6 Hz, respectively: Reference 12. Dybvig, D. H. *Inorg. Chem.* **1966**, *5*, 1795.

(15) This is based on a variety R$_f$OCF$_2$CF$_2$Cl, R$_f$OCF$_2$CX$_3$, and R$_f$OCX$_2$CF$_2$Cl derivatives where R$_f$ = CF$_3$O, CF$_3$SO$_2$, and CF$_3$C(O). See for example: Johri, K. K.; DesMarteau, D. D. *J. Org. Chem.* **1983**, *48*, 242. Tari, I.; DesMarteau, D. D. *Ibid.* **1980**, *45*, 1214.

(16) CF$_3$OOH is stable in clean glass at 22 °C, but it is quite sensitive to the presence of certain impurities (see ref 11).

(17) Details on the preparation of these compounds will be reported separately.

(18) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1979**, *18*, 919.

Figure 1. 94.1-MHz CW ^{19}F NMR (5 mm) of 15 mol % of Cl$_2$CFCF$_2$NCF$_2$O in CFCl$_3$.

tivity. Thus in the planned conversion of CF$_3$OOCF$_2$NHCF$_2$CFXCl to the respective oxaziridines, KHF$_2$ was the reagent of choice.

The reaction of excess KHF$_2$ with CF$_3$OOCF$_2$NHCF$_2$CFXCl at 22 °C gives excellent yields of the oxaziridines (eq 11). A minor byproduct in each

CF$_3$OOCF$_2$NHCF$_2$CFXC: + KHF$_2$ ⟶ ClXCFCF$_2$N—CF$_2$ + COF$_2$ +

$$\underset{\text{O}}{\diagdown\diagup}$$

KHF$_2$·HF   (11)

case is O=C=NCF$_2$CFXCl, which presumably arises from hydrolysis of the oxaziridine by small amounts of H$_2$O in the KHF$_2$. The latter is difficult to dry thoroughly. The mechanism of this reaction remains obscure,[18] but the generality of the reaction is more clear with the five examples now demonstrated.

Like the previous examples of perhalogenated oxaziridines CF$_3$NCF$_2$O[7] and SF$_5$NCF$_2$O,[8] these new oxaziridines are thermally stable but highly reactive. Their characterization is given in the Experimental Section. Their IR spectra exhibit strong absorptions near 1430 cm^{-1}, as well as absorptions near 1060 and 950 cm^{-1}, which are characteristic of the oxaziridine ring.[8] The CI mass spectra exhibit parent (MH)$^+$ ions for each compound and a variety of other ions which are supportive of the parent compound. The ^{19}F NMR, while quite complex, provide the most definitive proof of structure.

The experimental spectrum for Cl$_2$FCCF$_2$NCF$_2$O is shown in Figure 1. The spectra are clearly of the type ABCMN, where the fluorines labeled b–d in Figure 1

constitute the ABC portion and fluorines a and e the MN portion. The high inversion barrier of the nitrogen is responsible for the magnetic nonequivalence of fluorines b,c and d,e. The large value of J_{bc} = 190 Hz is quite comparable to that found for acyclic nitrogen compounds of the type R$_f$CF$_2$NClF and R$_f$CF$_2$NBrF where R$_f$ is a perfluoroalkyl group.[19] The very small value of J_{de} = 3.0 Hz is surprising but is similar to that in CF$_3$NCF$_2$O, where the ring methylene fluorines exhibit an apparent simple first-order spectrum.[7] The spectrum with X = Cl in OF$_2$CNCF$_2$CFXCl could be readily simulated by application of LAOCOON 3,[20] and the stated coupling constants are taken from this simulation. For X = F and Br, the overall appearance of the spectra are similar to that for X = Cl, but they are more complex. In the case of X = F, a reasonable simulation could only be achieved by assuming the two CF$_2$Cl fluorines to be nonequivalent. For X = Br, the two chiral centers give rise to a mixture of diastereoisomers differing somewhat in the chemical shifts and J_{FF} values. For the latter two compounds, a detailed analysis of the spectra would require a major effort, and we did not attempt this.

Conclusion

The practical use of CF$_2$=NCl to prepare a variety of 1,1-difluoro-2-azaperhalo-1-butenes by thermal addition to CF$_2$=CFX (X = F, Cl, Br) olefins has been demonstrated. These azabutenes can be converted to novel oxaziridines by oxidation of the C=N double bond with CF$_3$OOH via the intermediate adducts CF$_3$OOCF$_2$NHCF$_2$CFXCl followed by treatment with KHF$_2$. Both CF$_2$=NCF$_2$CFXCl and OF$_2$CNCF$_2$CFXCl are useful reagents for the synthesis of a variety of novel fluorochemicals, and these results will be reported separately.

(19) Chang, S. C.; DesMarteau, D. D. *Inorg. Chem.* 1983, 22, 805.
(20) Bothner-By, A. A.; Castellano, S. M. In "Computer Programs for Chemistry"; Detar, D. F., Ed., W. A. Benjamin: New York, 1968; Vol. 1, p 10.

Some Novel Reactions of N-Chlorodifluoromethanimine

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Some reactions of N-chlorodifluoromethanimine, CF_2=NCl, have been studied and are compared to related reactions of perfluoromethanimine, CF_2=NF. Fluoride promoted reactions of CF_2=NCl result in evidence for the CF_3NCl^- anion, which is thermally less stable and less reactive than CF_3NF^-. Oxidation of CF_3NCl^-, formed in situ by reaction of CF_2=NCl with KF or CsF, with Cl_2 forms CF_3NCl_2. With Br_2, CF_3NBrCl is formed along with CF_3NBr_2. The latter arises from a novel fluoride-catalyzed conversion of CF_3NBrCl to CF_3NBr_2 by Br_2, and the same products can be obtained starting with CF_3NCl_2, Br_2, and MF. Extension of this reaction to $C_2F_5NCl_2$ and $C_3F_7NCl_2$ is also discussed. Addition of $XOSO_2F$ (X = Cl, Br) to CF_2=NCl forms the novel diazene FSO_2OCF_2N=NCF_2OSO_2F, presumably via the intermediate FSO_2OCF_2NClX addition products. Competitive reaction of CF_2=NF and CF_2=NCl with fluoride ion results in the preferential formation of CF_3NF^-. Nucleophilic attack of the latter on CF_2=NCl forms the novel diaziridine $CF_3\overline{NCF_2N}Cl$, which can be reduced by Hg in trifluoroacetic acid to $CF_3\overline{NCF_2N}H$. The mechanism for the formation of the diaziridines is discussed.

Introduction

N-Chlorodifluoromethanimine, CF_2=NCl, was reported first in 1970.[2] However, there have been very few reports on the chemistry of this easily prepared imine.[3-5] In-

vestigations of the chemistry of the related imine CF_2=NF[6,7] led us to undertake studies of the reaction chemistry of CF_2=NCl. As was found for CF_2=NF, CF_2=NCl reacts readily with electrophilic halogen sources. Similarly, CF_2=NCl reacts with fluoride ion from CsF and KF to form the anion CF_3NCl^-. However, the products of the reactions involving CF_2=NCl are often different from those of CF_2=NF. These differences are easily explained by the photochemical and thermal instability of the

(1) Visiting Scholar, Peoples Republic of China.
(2) Young, D. E.; Anderson, L. R.; Fox, W. B. *J. Chem. Soc., Chem. Commun.* 1970, 395.
(3) Young, D. E.; Anderson, L. R.; Fox, W. B. U.S. Patent 3 689 563; *Chem. Abstr.* 1972, 78, 29213.
(4) Swindell, R. F.; Zaborowski, L. M.; Shreeve, J. M. *Inorg. Chem.* 1971, 10, 1635.
(5) Zheng, Y. Y.; DesMarteau, D. D. *J. Org. Chem.* 1983, 48, 4844.

(6) Chang, S.-C.; DesMarteau, D. D. *J. Org. Chem.* 1983, 48, 771.
(7) Chang, S.-C.; DesMarteau, D. D. *Inorg. Chem.* 1983, 22, 805.

products arising from $CF_2=NCl$, and by an apparent lower reactivity of CF_3NCl^- as a nucleophile in comparison with CF_3NF^-.

In the course of this research, a novel catalytic conversion of N–Cl bonds to N–Br bonds by alkali metal fluorides and bromine was found.[8] Some details of this reaction are also presented. Two new compounds CF_3CF_2NBrCl and $CF_3CF_2CF_2NBrCl$ obtained via this reaction provide an opportunity to compare the effects of halogen substitution on nitrogen inversion barriers.

Experimental Section

General Methods. All manipulations of volatile compounds were carried out in Pyrex and stainless steel vacuum systems equipped with glass–Teflon and Teflon-packed stainless steel valves, respectively. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Amounts of reactants and products were measured by PVT measurements or by direct weighing. Temperatures were measured using a digital-indicating iron-constant thermocouple.

IR spectra were recorded on Perkin-Elmer 1330 or 1430 Data Systems employing a 10-cm gas cell fitted with AgCl or KCl windows, at pressures from 5 to 100 torr. NMR spectra were taken on a Varian XL-100-15 spectrometer using 85 mol % $CFCl_3$ as a solvent and internal reference, or on a JEOL FX-90Q spectrometer using 1 mol % compound in CCl_4 solvent, containing 20 mol % $CDCl_3$ as an internal ^2H lock and 1 mol % $CFCl_3$ as an internal standard. ^{19}F chemical shifts at lower frequency than $CFCl_3$ are negative. Mass spectra were recorded on Finnigan 4021-C or Hewlett-Packard 5985-B spectrometers at 70 eV for both EI and CI (CH_4). Samples were introduced by direct gas injection.

Melting points were measured by a modified Stock technique. Molecular weights were determined by vapor density measurements using a calibrated 0.2-L Pyrex bulb fitted with a glass–Teflon valve. Vapor pressures as a function of temperature were determined by the method of Kellogg and Cady.[9] Data were analyzed by a least-squares fit to both linear and quadratic equations, and the best fit is reported.

GLC purification of selected compounds was carried out on a Victoreen 4000 gas chromatograph equipped with gas injection, low temperature sample collection, and thermal conductivity detection. Stainless steel columns ($^3/_8$ in. OD) of appropriate length, packed with 35% Halcarbon 11-21 polymer oil on Chromosorb P, were employed.

Reagents. The compounds $CF_2=NF$,[10] $CF_2=NCl$,[2,5] $C_2F_5NCl_2$, $C_3F_7NCl_2$,[12] FSO_2OX (X = Cl, Br),[12,13] and CF_3SO_2OCl[14] were prepared by literature methods. Chlorine monofluoride was prepared by heating equimolar amounts of Cl_2 and F_2 in a Monel bomb for 18 h at 250 °C. Fluorine was obtained from Air Products and Chemicals, Inc. and was passed through a NaF scrubber before use. The metal fluorides KF and CaF were fused in a Pt crucible and then ground to a fine powder under very anhydrous conditions. All other reagents were readily available from commercial sources and were appropriately purified as needed before using.

Caution! Many of the starting materials and products of the reactions described in this research are potentially hazardous. Nearly all the materials described are potent oxidizers and some may be explosive. We have not encountered any difficulties in the course of this research for the quantities indicated, but due caution must be exercised when working with these materials.

Reaction of $CF_2=NCl$ with FSO_2OX (X = Cl, Br). In a typical reaction, $CF_2=NCl$ (2.1 mmol) was added by vacuum transfer to a 100-mL glass reactor at -196 °C. An equimolar

amount of FSO_2OX was then similarly added, and the reactor was allowed to warm to 22 °C in the air and stand for 1 day. The reactor was then cooled to -196 °C and checked for volatiles at this temperature. Nitrogen, 0.24 mmol and 0.46 mmol, was formed with X = Cl and Br, respectively. The content of the reactor was then pumped on through traps at -40, -80 and -196 °C, as it warmed in the air to 22 °C. The -196 °C trap contained Cl_2 (X = Cl) and Cl_2, BrCl, Br_2 (X = Br), and other unidentified fluorocarbon containing materials. The -80 °C trap contained a small amount of $(FSO_2OCF_2N)_2$ and an unidentified fluorosulfate derivative. The -40 °C trap contained 0.61 mmol (X = Cl) and 0.40 mmol (X = Br) of nearly pure $(FSO_2OCF_2N)_2$: mp -65.5 to -64.5 °C; M_r 326.0, calcd 326.15; IR 1925 (w), 1490 (s), 1250 (s), 1203 (s), 1116 (s), 1026 (m), 954 (s), 931 (s), 838 (s), 772 (m), 672 (vw), 599 (s), 551 (w), 473 (w) cm^{-1}; major m/z [CI] 327 (MH$^+$), 227 (M – SO$_3$F$^+$), 164 (FSO$_3$CF$_2$NH$^+$), 114 (CF$_2$SO$_2^+$), 67 (FSO$^+$); [EI] 149 (FSO$_3$CF$_2^+$), 128 (CF$_2$NNCF$_2$), 114 (CF$_2$SO$_2^+$), 85 (CF$_2$O$^+$), 83 (CFSO$_2$)$^+$, 69 (CF$_3^+$), 66 (CF$_2$O$^+$), 50 (CF$_2^+$), 47 (FCO$^+$); NMR 49.6 (t, SF), -73.5 (d, CF$_2$, $^4J_{FF}$ = 7.5 Hz).

Reactions of $CF_2=NCl$ in the Presence of Metal Fluorides. Reactions were carried out in 100-mL glass flasks fitted with a glass–Teflon valve and containing a small Teflon-coated magnetic stirring bar. The appropriate amount of active metal fluoride was added to the reactor in the glovebox and the reactor was then evacuated. After cooling to -196 °C, the gaseous reactants were added by vacuum transfer and the reactor was then warmed to 22 °C and stirred for an appropriate time in the dark. Products were then separated by vacuum fractionation through low temperature traps and by GLC with the exclusion of light. In the case of reactions involving Br_2, excess Br_2 was removed by brief treatment of the –NClBr and –NBr$_2$ fractions with $CH_2=CH_2$ at 22 °C, followed by reseparation from the $BrCH_2CH_2Br$ formed. Details of the reactions are summarized in Table I and II; characterization of new compounds follows.

CF_3NClBr: mp -62 °C; IR 1248 (s), 1218 (vs), 1178 (vs), 1116 (w), 1025 (vw), 893 (w), 787 (m), 688 (m) cm^{-1}; NMR -72.3 (s); major m/z [CI] 202/200/198 (MH$^+$), 201/199/197 (M$^+$), 182/180/178 (M – F$^+$), 148/144 (MH – Cl$^+$), 121/119 (MH – Br$^+$), 102/100 (CF$_2$NClH$^+$), 69 (CF$_3^+$); [EI] 201/199/197 (M$^+$), 145/143 (CF$_2$NBr$^+$), 101/99 (CF$_2$NCl$^+$), 95/93 (NBr$^+$), 69 (CF$_3^+$).

CF_3NBr_2: mp -56 °C; IR 1240 (s), 1211 (vs), 1168 (vs), 1089 (w), 1028 (w), 969 (vw), 890 (vw), 758 (m), 675 (m) cm^{-1}; NMR -70.5 (s); major m/z [CI] 246/244/242 (MH$^+$), 245/243/241 (M$^+$), 226/224/222 (M – F$^+$), 69 (CF$_3^+$); [EI] 245/243/241 (M$^+$), 145/143 (CF$_2$NBr$^+$), 95/93 (NBr$^+$), 69 (CF$_3^+$).

C_2F_5NClBr: IR 1336 (s), 1234 (w), 1188 (vs), 1149 (vs), 1071 (vs), 970 (vw), 902 (vw), 839 (w), 753 (w), 718 (m), 694 (m), 653 (w), 601 (w), 532 (w) cm^{-1}; NMR -77.8 (t, CF$_3$), -96.3 (q, CF$_2$, $^3J_{FF}$ = 1.0 Hz); major m/z [CI] 251/249/247 (M$^+$), 232/230/228 (M – F$^+$), 196/194 (C$_2$F$_4$NBrH$^+$), 152/150 (C$_2$F$_4$NClH$^+$), 69 (CF$_3^+$); [EI] 195/193 (C$_2$F$_4$NBr$^+$), 182/180/178 (CF$_2$NBrCl$^+$), 151/149 (C$_2$F$_4$NCl$^+$).

C_3F_7NClBr: IR 1342 (m), 1276 (m), 1242 (vs), 1230 (vs), 1200 (s), 1177 (m), 1132 (s), 1110 (s), 983 (s), 964 (s), 829 (w), 806 (w), 753 (m), 703 (w), 678 (w), 666 (w), 601 (w), 531 (w) cm^{-1}; NMR $CF_3{}^ACF_2{}^BCF_2{}^CNBrCl$ A -82.2 (t), B -119.7 (t), C -87.9 (q-t, J_{AB} 1.0, J_{AC} = 9.0, J_{BC} = 2.0 Hz); major m/z [CI] 301/299/297 (M$^+$), 282/280/278 (M – F$^+$), 182/180/178 (CF$_2$NBrCl$^+$), 119 (C$_2$F$_5^+$), 69 (CF$_3^+$); [EI, 17 eV] 301/299/297 (M$^+$), 245/243 (M – FCl$^+$), 201/199 (M – BrF$^+$), 182/180/178 (CF$_2$NClBr$^+$), 119 (C$_2$F$_5^+$).

$\overline{CF_3NCF_2NCl}$: bp 15.3 °C; mp -120 °C; M_r 182.0, calcd 182.48; log P (torr) = 7.7071 - 1392.05/T - (1432 × 10^2/T^2); ΔH vap = 6.37 Kcal/mol; ΔS vap = 22.1 eu; IR 1411 (vs), 1295 (vs), 1211 (vs), 1133 (w), 1048 (s), 979 (s), 827 (w), 770 (m), 742 (w), 677 (s), 571 (w), 517 (w) cm^{-1}; NMR $CF_3{}^MNCF^AF^BNCl$ M -64.9 (d), A -112.4 (m), B -106.3 (m, J_{AB} = 32.5, J_{AM} 12.0 Hz); major m/z [CI] 185/183 (MH$^+$), 147 (M – Cl)$^+$, 134 (C$_2$F$_5$NH$^+$), 91 (C$_2$F$_2$N$_2$H$^+$), 87/85 (CF$_2$Cl$^+$), 69 (CF$_3^+$); [EI] 114 (C$_2$F$_4$N$^+$), 87/85 (CF$_2$Cl$^+$), 69 (CF$_3^+$), 50 (CF$_2^+$), 51/49 (NCl$^+$).

Synthesis of $\overline{CF_3NCF_2NH}$. In a typical reaction, a 100-mL flask fitted with a glass–Teflon valve and containing 2.5 g of Hg and a small magnetic stirring bar was cooled to -196 °C and evacuated. Trifluoroacetic acid (6.5 mmol) was added by vacuum transfer, followed by CF_3NCF_2NCl (1.0 mmol). The reactor was

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(10) Sekiya, A.; DesMarteau, D. D. *J. Org. Chem.* **1981**, *46*, 1277.

(11) Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.

(12) Roberts, J. E.; Cady, G. H. *J. Am. Chem. Soc.* **1960**, *82*, 352. (A small excess of $S_2O_6F_2$ was employed).

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(14) Katsuhara, Y.; Hammaker, R. M.; DesMarteau, D. D. *Inorg. Chem.* **1980**, *19*, 607.

Table I. Fluoride Promoted Reactions of CF_2=NCl[a]

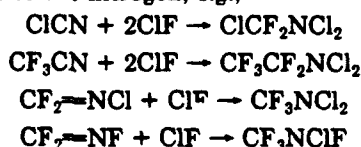| CF_2=NCl	reactant	MF	time, 22 °C[c]	products[b]
2.0	Cl_2 (5.0)		2 d	no reactn
2.0	Br_2 (5.0)		2 d	no reactn
2.0	BrCl (5.0)		2 d	no reactn
13.0		CsF (13)	1 d	CF_3NCl_2 (4.6)
2.0	Cl_2 (2.3)	CsF (10)	2 d (55 °C)	CF_3NCl_2 (1.5)
2.0	BrCl (6.0)	CsF (10)	1 d	CF_3NCl_2 (1.96)
2.0	Br_2 (4.0)	CsF (9.2)	11 h	CF_3NBrCl (0.68), CF_3NBr_2 (0.55), CF_3NCl_2 (0.18)
1.0	Br_2 (7.0)	CsF (7.0)	12 h	CF_3NBrCl (0.22), CF_3NBr_2 (0.30), CF_3NCl_2 (?)
2.0	Br_2 (1.7)	CsF (8.5)	11 h	CF_3NBrCl (0.43), CF_3NCl_2 + CF_2=NCl (1.2)
2.0	Br_2 (2.0)	CsF (20)	12 h	CF_3NClBr (0.78), CF_3NCl_2 (0.45)
4.2	Br_2 (10)	CsF (10)	3 d	CF_2NClBr (.49), CF_3NBr_2 (2.2), CF_3NCl_2 (.31)
4.5	Br_2 (10)	KF (10)	2 d	CF_3NClBr (.78), CF_3NBr_2 (2.4), CF_3NCl_2 (0.4)
3.0	Br_2 (3.0)	NaF (10)	2 d	no reactn
2.8	CF_2=NF (3.6)	CsF (13)	3.5 h	$CF_3\overline{NCF_2NCl}$ (0.8), CF_3NClF, CF_3NCl_2, $CF_3\overline{NCF_2NF}$

[a] Amounts in mmol. Reactions carried out in the absence of light. [b] Some CF_2=NCl absorbed by MF. [c] d = days

then held at 10 °C for 2 h with stirring. The reactor was then cooled to −196 °C and a small amount of N_2 was removed. The vessel was then pumped on through traps at −78, −110, and −196 °C as it warmed in the air. The −78 °C trap collected CF_3CO_2H, the −196 °C trap contained unreacted starting material, and the −110 °C trap contained a mixture of the N–Cl and N–H diaziridines. This was reseparated by passing it through −100 and −196 °C traps to yield 0.48 mmol of $CF_3\overline{NCF_2NH}$ in the −100 °C trap: IR 3319 (m), 1517 (w), 1452 (vs), 1371 (w), 1327 (vs), 1269 (vs), 1231 (vs), 1177 (s), 1086 (s), 1040 (s), 934 (s), 825 (w), 739 (w), 681 (m), 520 (w) cm^{-1}; NMR $CF_3^M NCF^A F^B N^X H$ M −65.5 (dd), A −119.2 (m), B −98.0 (m), X (Me_4Si), 4.2 (br s, J_{AM} = 14.0, J_{BM} = 3.5, J_{AB} = 46.0, J_{AX} = 14, $J_{MX} \simeq J_{BX} \simeq 0$ Hz); major m/z [CI] 149 (MH$^+$), 129 (M − F$^+$); [EI] 128 (M − HF$^+$), 109 ($C_2F_3N_2^+$), 69 (CF_3^+).

Results and Discussion

Reaction of CF_2=NCl with FSO_2OX (X = Cl, Br). The addition of electrophilic halogen compounds to halogenated substrates containing carbon–nitrogen multiple bonds is now a well established reaction. Most examples involve reaction of ClF, where the formal positive chlorine always adds to the nitrogen, e.g.,[15]

$$ClCN + 2ClF \rightarrow ClCF_2NCl_2$$

$$CF_3CN + 2ClF \rightarrow CF_3CF_2NCl_2$$

$$CF_2=NCl + ClF \rightarrow CF_3NCl_2$$

$$CF_2=NF + ClF \rightarrow CF_3NClF$$

With CF_2=NF, we found that FSO_2OX (X = Cl, Br, OSO_2F) underwent a similar facile addition, and in the case of X = Br, gave the first example of an −NBrF derivative in FSO_2OCF_2NBrF.[7] We therefore undertook a study of the reactions of FSO_2OX (X = Cl, Br) with CF_2=NCl in hope of isolating FSO_2OCF_2NBrCl, as the first example of an −NBrCl derivative.

Both FSO_2OCl and FSO_2OBr react readily with CF_2=NCl at 22 °C. Unlike CF_2=NF, however, the expected addition product is not isolated. Instead, both reactions give a moderate yield of the diazene FSO_2OCF_2N=NCF$_2OSO_2F$. Since both −NCl$_2$[11] and −NClBr[8] derivatives are known to decompose both thermally and photolytically to diazenes, these reactions can be rationalized as follows.

$$FSO_2OX + CF_2=NCl \rightarrow \text{“}FSO_2OCF_2NClX\text{”} \xrightarrow{-XCl} FSO_2OCF_2N=NCF_2OSO_2F$$
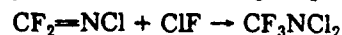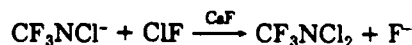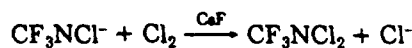
$$X = Cl, Br$$
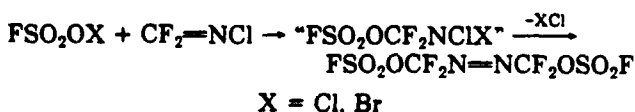
However, it is surprising that an −NCl$_2$ derivative would undergo this reaction so readily, based on the usual properties of such compounds. Either the fluorosulfate group has a pronounced effect on the N–X bond, or the reaction path leading to the observed diazene does not involve the sample addition of FSO_2OX to the C=N bond as indicated above.

Attempts to extend this reaction by the use of CF_3SO_2OCl were unsuccessful. Instead of the anticipated addition product or the diazene ($CF_3SO_2OCF_2N$=)$_2$, the slow reaction below 0 °C resulted in the formation of large amounts of CF_3Cl, Cl_2, and polymeric products. This result was unexpected because FSO_2OCl and CF_3SO_2OCl often lead to analogous products in addition to unsaturated compounds such as olefins and SF_4.[15,16] However, if a radical species containing the CF_3SO_3 group is formed in the initial reaction or in the subsequent decomposition of an intermediate, the rapid loss of CF_3 from this radical can be expected to lead to CF_3Cl and other products. This presumption is based on the apparent general instability of free-radicals of the type CF_3SO_2M. This the photolysis or thermal decomposition of compounds such as RSO_2OCl, (RSO_2)$_2NCl$, (RSO_2O)$_2$, and (RSO_2O)$_2Xe$, where R = CF_3 or F, does not lead to analogous products. For example, photolysis of (RSO_2)$_2NCl$ gives (FSO_2)$_2N$–N(SO_2F)$_2$ and Cl_2 for R = F and $O_2SNSO_2CF_3$ and CF_3Cl for R = CF_3.[17]

Fluoride Promoted Reactions of CF_2=NCl. Reactions of CF_2=NCl in the presence of fluoride ion from KF or CsF provide ample evidence for the formation of the N-chlorotrifluoromethanamine ion, CF_3NCl^-. This anion is apparently less stable than CF_3NF^-, formed analogously from CF_2=NF.[6,7,18] As shown in Table I, the reaction of CF_2=NCl with CsF alone leads to CF_3NCl_2[19] as the only volatile product. This clearly results from a decomposition of the anion forming either Cl_2 or ClF, which then reacts with CF_3NCl^- or CF_2=NCl to form the observed CF_3NCl_2.

$$CF_2=NCl + F^- \xrightarrow{CsF} CF_3NCl^- \rightarrow ? + Cl_2 \text{ or } ClF$$

$$CF_3NCl^- + Cl_2 \xrightarrow{CsF} CF_3NCl_2 + Cl^-$$

$$CF_3NCl^- + ClF \xrightarrow{CsF} CF_3NCl_2 + F^-$$

$$CF_2=NCl + ClF \rightarrow CF_3NCl_2$$

The decomposition product resulting in the Cl_2 and/or ClF has not been identified. On a larger scale the CsF becomes tacky, indicating the possible formation of a polymeric material.

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When a mixture of CF_2=NCl and Cl_2 is allowed to react in the presence of CsF the intermediate CF_3NCl^- anion is rapidly oxidized to give a much improved yield of CF_3NCl_2. At 55 °C the yield is improved to 75%, although it is now clear that this yield will depend on the amount of Cl_2 and CsF used. It was also found that BrCl was even more effective than Cl_2 in this oxidation. As shown in Table I, a nearly quantitative conversion was found.
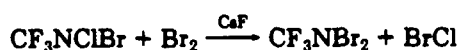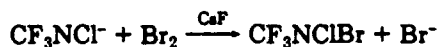
$$CF_3NCl^- + BrCl \xrightarrow{CsF} CF_3NCl_2 + Br^-$$
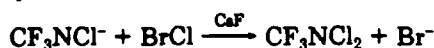
It appears that this reaction actually proceeds via the initial formation of CF_3NBrCl as shown in the following equation.

$$CF_3NCl^- + BrCl \xrightarrow{CsF} CF_3NBrCl + Cl^-$$
$$\downarrow BrCl$$
$$CF_3NCl_2 + Br_2$$
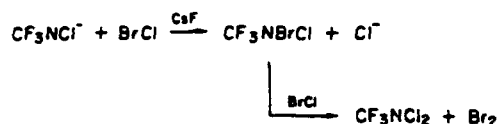
This is based on the fact that the Br in BrCl should be the electrophile and that in separate reactions of CF_3NBrCl with excess BrCl in the absence of CsF, CF_3NCl_2 is formed in quantitative yield (see next section).
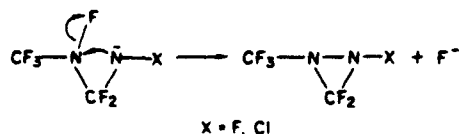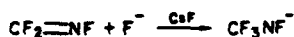
The use of Br_2 to oxidize the CF_3NCl^- anion leads to good yields of CF_3NClBr, along with the formation of CF_3NCl_2 and CF_3NBr_2. As shown in Table I, the relative yields depend strongly on the relative amounts of Br_2 and CsF employed. Sodium fluoride is ineffective in this reaction, because the NaF is too weak a fluoride base to generate the CF_3NCl^- anion from CF_2=NCl. On the other hand, KF is as effective as CsF. The formation of both CF_3NCl_2 and CF_3NBr_2 depend on the formation of BrCl and on the fluoride catalyzed conversion of CF_3NClBr to CF_3NBr_2 by Br_2 (see following section).

$$CF_3NCl^- + Br_2 \xrightarrow{CsF} CF_3NClBr + Br^-$$

$$CF_3NClBr + Br_2 \xrightarrow{CsF} CF_3NBr_2 + BrCl$$

$$CF_3NBr_2 \xrightarrow{BrCl} CF_3BrCl \xrightarrow{BrCl} CF_3NCl_2$$

A large excess of Br_2 clearly increases the yield of CF_3NBr_2 and decreases the amount of CF_3NClBr and CF_3NCl_2.

Attempts to use CF_3NCl^- as a nucleophile in nucleophilic substitution reactions were unsuccessful. Reactions of CF_2=NCl with $R_fC(O)F$ in the presence of CsF, which were successful with CF_3NF^- anion,[6] led to the CF_3NCl_2 and unreacted $R_fC(O)F$. This may mean that CF_3NCl^- is considerably less nucleophilic than CF_3NF^-, but it may also only serve to indicate that the rate of decomposition of CF_3NCl^- is faster than the intended nucleophilic substitution on $R_fC(O)F$.

A competitive reaction involving CF_2=NF and CF_2=NCl indicates that CF_3NF^- is formed preferentially to CF_3NCl^-, and the former is then sufficiently reactive to attack CF_2=NCl. The observed products are then easily explained based on the known chemistry of CF_2=NF.[6]

$$CF_2=NF + F^- \xrightarrow{CsF} CF_3NF^-$$

$$CF_3NF^- + CF_2=NX \longrightarrow CF_3NFCF_2NX^- \underset{F^-}{\overset{-F^-}{\rightleftharpoons}} CF_3NFCF=NX$$

X = F, Cl

The intermediate formamidine CF_3NFCF=NX was readily isolated in the case of X = F, but we could not isolate CF_3NFCF=NCl, presumably because of different reaction rates for the formation and cyclization of formamidine when X = F vs. X = Cl.

The conversion of 1-chloro-2-(trifluoromethyl)-3,3-difluorodiaziridine to the 1-hydro derivative was accomplished in low yield by reaction with Hg in trifluoroacetic acid (TFA).
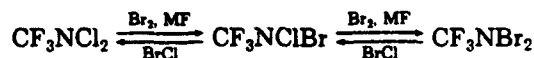
$$CF_2N-CF_2 + Hg + CF_3CO_2H \xrightarrow{TFA} CF_3N-CF_2 + CF_3C(O)OHgCl$$
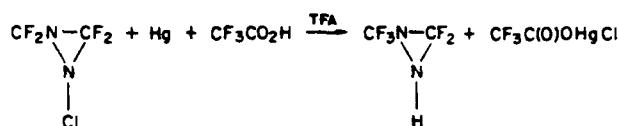
This reaction is analogous to the conversion of R_fNClF to R_fNHF in the same manner.[10] In the latter reaction, substitution of trifluoroacetic anhydride (TFAA) for the acid gives excellent yields of the *N*-fluoroimines $R_f'CF$=NF. However, the same reaction with the 1-chlorodiaziridine gave CF_3N=CF_2 and N_2 as the major products, suggesting that the intermediate 2-diazirine, if formed, is unstable under the reaction conditions.

$$CF_3-N-CF_2 \xrightarrow{Hg, TFAA} {}^{\cdot}CF_3-N-CF^{\cdot} \longrightarrow CF_3N=CF_2 + N_2$$
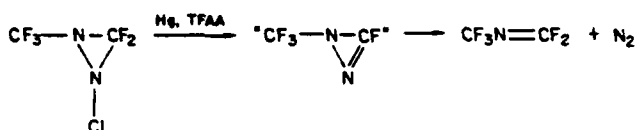
Fluoride-Catalyzed Reactions of R_fNClX (X = Cl, Br) with Br_2. The formation of CF_3NBr_2 in the reaction CF_2=NCl with Br_2 in the presence of CsF, indicated that an N–Cl bond in CF_3NClBr was converted to an N–Br bond by an unknown reaction type. At first BrCl was assumed to be responsible, but as shown in the following equation this was clearly not the case.

$$CF_3NCl_2 + Br_2 \leftarrow CF_3NClBr + BrCl \nrightarrow CF_3NBr_2 + Cl_2$$

It was soon evident that the metal fluoride was directly involved in the reaction and surves as a catalyst for this conversion. The way in which the metal fluoride functions as a catalyst or promoter of this reaction is still unknown. The data in Table II clearly establish that alkali metal fluorides are effective and other materials such as CaF_2 and activated charcoal are not. As we have disucssed in a preliminary communication, a polyhalide anion may be involved.[8] The data in Table II may be summarized by the following reaction scheme.

$$CF_3NCl_2 \underset{BrCl}{\overset{Br_2, MF}{\rightleftharpoons}} CF_3NClBr \underset{BrCl}{\overset{Br_2, MF}{\rightleftharpoons}} CF_3NBr_2$$

Depending on the starting material, CF_3NCl_2 or CF_3NBrCl, the relative amount of BrCl is greater for CF_3NCl_2 and this decreases the amount of CF_3NBr_2 formed. Previously, we reported that only CsF leads to the formation of CF_3NBr_2.[8] This is clearly not the case if one starts with CF_3NBrCl, where both NaF and KF also yield CF_3NBr_2. The different results starting with CF_3NCl_2 can be explained by proposing that a larger amount of free BrCl is present in the case of KF or NaF. The very active CsF used in this work readily absorbs Br_2 and probably BrCl, whereas the absorption of Br_2 by KF is much less, and almost negligible by NaF.

The fluoride-promoted conversion of N–Cl bonds to N–Br bonds by Br_2 is a general reaction and has been extended to several other NCl_2 derivatives. Starting with R_fCN and ClF, this method should allow the preparation of a variety of $NClBr$ and NBr_2 derivatives.
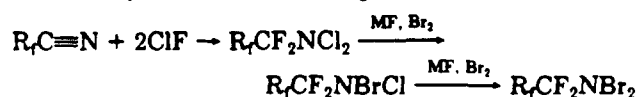
$$R_fC\equiv N + 2ClF \rightarrow R_fCF_2NCl_2 \xrightarrow{MF, Br_2}$$

$$R_fCF_2NBrCl \xrightarrow{MF, Br_2} R_fCF_2NBr_2$$

Table II. Fluoride Promoted Reactions of R_fNClX (X = Cl, Br)[a]

R_fNClX[a]	reactant	MF	time, 22 °C[a]	products
CF_3NCl_2 (0.5)	Br_2 (5.0)		2 d	no reactn[b]
CF_3NCl_2 (0.5)	BrCl (0.5)		2 d	no reactn[b]
CF_3NClBr (0.7)	Br_2 (1.4)		12 h	no reactn[b]
CF_3NClBr (0.7)	BrCl (2.8)		12 h	CF_3NCl_2 (0.7)
CF_3NCl_2 (1.0)	Br_2 (10)	CaF (10)	42 h	CF_3NClBr (0.2), CF_3NBr_2 (0.3)[b]
CF_3NCl_2 (1.0)	Br_2 (10)	CaF (20)	40 h	CF_3NClBr (0.3), CF_3NBr_2 (0.1)[b]
CF_3NCl_2 (1.0)	Br_2 (10)	KF (10)	40 h	CF_3NClBr (0.4), CF_3NBr_2 (trace)[b]
CF_3NCl_2 (1.0)	Br_2 (10)	NaF (10)	40 h	CF_3NClBr (0.5)[b]
CF_3NCl_2 (1.0)	Br_2 (10)	LiF (10)	40 h	CF_3NClBr (0.2)[b]
CF_3NCl_2 (1.0)	Br_2 (10)	CaF_2 (10)	40 h	no reactn[b]
CF_3NCl_2 (1.1)	Br_2 (10)	Charcoal (0.5g)	2 d	CF_3NCl_2, other
CF_3NClBr (1.0)	Br_2 (10)	NaF (15)	2 d	CF_3NBrCl (0.28), CF_3NBr_2 (0.13), CF_3NCl_2 (0.15)
CF_3NClBr (1.1)	Br_2 (10)	KF (10)	2 d	CF_3NBrCl (0.39), CF_3NBr_2 (0.35), CF_3NCl_2 (0.24)
CF_3NClBr_2 (0.6)	Br_2 (10)	CaF (10)	12 h	CF_3NBr_2 (0.5), CF_3NBrCl, CF_3NCl_2
CF_3NClBr (0.5)	Br_2 (1.0)	CaF (20)	12 h	CF_3NBr_2 (0.1), CF_3NClBr (0.3), CF_3NCl_2 (0.1)
$C_2F_5NCl_2$ (1.0)	Br_2 (10)	CaF (10)	40 h	C_2F_5NClBr (0.4), $C_2F_5NBr_2$ (0.2)[b,c]
$C_3F_7NCl_2$ (1.7)	Br_2 (11)	CaF (10)	40 h	C_3F_7NBrCl + $C_3F_7NBr_2$ (0.7)[b,d]

[a] Amounts in mmol. All reactions carried out in the absence of light. d = days. [b] Recovered starting $-NCl_2$. [c] $C_2F_5NBr_2$ identified by ^{19}F NMR and mass spectrum. See ref 20. [d] $C_3F_7NBr_2$ identified only by mass spectrum with intense M^+ in both EI and CI. See discussion.

Table II shows data for $CF_3CF_2NCl_2$ and $CF_3CF_2CF_2NCl_2$. In both cases, some of the respective NBr_2 derivatives were also formed, but the latter could not be readily isolated as pure compounds from the $BrCH_2CH_2Br$ formed on removal of excess Br_2 by treatment with ethylene. *N,N*-dibromoperfluoropropanamine was identified only by its mass spectrum and $CF_3CF_2NBr_2$ by its mass spectrum and ^{19}F NMR. The latter agreed with a published NMR spectrum.[20]

Characterization of New Compounds. The data given in the experimental section provides excellent support for the indicated structures. No direct spectroscopic evidence for the N–N double bond in $FSO_2OCF_2N{=}NC{-}F_2OSO_2F$ is given, but the mass spectrum clearly identifies the presence of two nitrogens in the molecule. For $CF_3\overline{NCF_2N}X_2$ (X = Cl, H), the ring structure is clearly evident by comparison of the IR and NMR with $CF_3\overline{N{-}CF_2NF}$.[6] Both diaziridines appear to be present in only one isomeric form as an enantiomeric pair of either the cis or trans diastereomers. On steric grounds the favored isomer should be trans, but our data do not allow an assignment to be made. However, the isomers are probably the same as $CF_3\overline{NCF_2NF}$, which can be reasonably assigned as trans based on the magnitudes of the CF_3–NF $^4J_{FF}$ coupling.[6] The syntheses of CF_3NBrCl and CF_3NBr_2 complete the series CF_3NXX' (X, X' = F, Cl, Br). No *N*-iodo derivatives have been reported and we have thus far been unable to extend our reactions to iodine. The new compounds exhibit surprisingly high thermal stability, with CF_3NBr_2 (g, 100 torr) stable to at least 100 °C in glass. At near 140 °C, CF_3NBr_2 undergoes extensive decompostion to $CF_3N{=}NCF_3$ and Br_2. On the other hand, pure CF_3-$NBrCl$ (g, 100 torr) was stable to 160 °C, but suddenly decomposed to $CF_3N{=}NCF_3$ and other products at ~175 °C. The stability of CF_3NBrCl is strongly influenced by impurities (presumably Br_2) and impure samples were observed to slowly form CF_3NBr_2 and CF_3NCl_2 at 50 °C.

Both CF_3NBrCl and CF_3NBr_2 are yellow gases and are very sensitive to Pyrex filtered sunlight, forming the diazene $CF_3N{=}NCF_3$[21] in high yield.

$$2CF_3NBrX \xrightarrow{h\nu} CF_3N{=}NCF_3 + 2XBr$$

$$X = Cl, Br$$
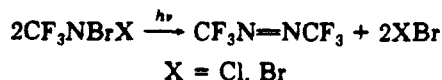
Table III. Some Properties of CF_3NXX'

CF_3NX_2	δ CF$_3$ (CFCl$_3$)	NX, cm^{-1}
CF_3NF_2[22]	-84.1	1018, 951[a]
CF_3NFCl[19]	-79.3[b]	951, 752[a]
CF_3NFBr[7]	-77.6	934, 731[b]
CF_3NCl_2[11]	-74.1[b]	812, 708[b]
CF_3NClBr	-72.3[b]	787, 688[b]
CF_3NBr_2	-70.5[b]	758, 675[b]

[a] Assignments taken from Schack, C. J.; Christe, K. O. *Inorg. Chem.* 1983, *22*, 22. [b] This work.

This is in contrast to all other members of the CF_3NXX' series, which are essentially stable to photolysis under the same conditions. In Table III, some comparative data for CF_3NXX' are shown. The trends in Table III are remarkably regular. A simple plot of the CF_3 chemical shift vs. the sum of the Pauling electronegativities of X is essentially linear. In CF_3NClBr, the two N–X stretches must be strongly coupled, otherwise it is hard to understand why the ν (NCl) stretch would be higher than the average of the symmetric and assymmetric ν (NCl) stretches in CF_3NCl_2, and ν (NBr) lower than the same average in CF_3NBr_2.

Finally, the NMR for CF_3CF_2NClBr and $CF_3CF_2CF_2N$-$ClBr$ are rather surprising. All known perhalogenated derivatives of the type RCF_2NFX (X = Cl, Br, FSO_3 and R = R_x, Cl, FSO_3) exhibit pronounced second-order AB spectra for the methylene fluorines,[4,6,23] due to the high inversion barrier and resultant chiral nitrogen. In contrast, CF_3CF_2NBrCl and $CF_3CF_2CF_2NBrCl$ exhibit apparent first-order NMR spectra. These observations leave only two possibilities concerning the inversion at nitrogen; the substitution of a fluorine atom on nitrogen by either chlorine or bromine lowers the inversion varrier, so that inversion is rapid on the NMR time scale at 22 °C, or the inversion is slow on the NMR time scale, but the diastereotopic α-methylene fluorine atoms have identical or nearly identical chemical shifts leading to a very large J/Δ and the apparent first-order spectra.[24]

Recent work on inversion barriers of acylic nitrogen compounds indicates that two electronegative substituents on nitrogen are required to have an inversion barrier of

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(24) See: Corio, P. L. "Structure of High-Resolution NMR Spectra"; Academic Press: New York, 1966.

~23 kcal/mol and thus configuration stability at 22 °C.[25] These authors claim a lower limit of ~7.1 for the sum of the electronegativities of CH_3O and X in $MeCO_2CH_2$-$(CH_3)_2CN(X)OMe$. The related series, $CF_3N(F)CF_2CF_3$,[22] $ClCF_2CF_2N(Cl)CF_3$,[26] CF_3CF_2NFCl,[23] CF_3CF_2NFBr,[7] and $FSO_2OCF_2N(F)OSO_2F$,[7] provides an interesting comparison in this regard. If the contribution of the alkyl groups C_2F_5, $ClCF_2CF_2$, and FSO_2OCF_2 are all similar, the sum of the electronegativities of the other two substituents on nitrogen can be compared. Since the electronegativity of the CF_3 group is near 3.3 on the Pauling scale,[27] and that of FSO_2O is close to 3.8,[16c] the sums for the aforementioned five compounds are 7.3, 6.5, 7.2, 7.0, and 7.8, respectively, but only the last three compounds exhibit configuration stability at 22 °C. Clearly, the prediction of inversion barriers on the basis of the electronegativities of the substituents on nitrogen is only a very approximate guide.

In the near future, we hope to prepare $ClCF_2CF_2N$-$(X)OCF_3$ (X = F, Cl). These two compounds would provide interesting insight into the effect of electronegativities on inversion barriers in acyclic nitrogen compounds. The CF_3O group has a value of at least 3.8.[28]

Registry No. CF_2=NCl, 28245-33-2; CF_3NCl_2, 13880-73-4; CF_3NClBr, 88453-17-2; $C_2F_5NCl_2$, 677-66-7; $C_3F_7NCl_2$, 662-54-4; FSO_2OCl, 13997-90-5; FSO_2OBr, 13997-93-8; Cl_2, 7782-50-5; Br_2, 7726-95-6; BrCl, 13863-41-7; CF_2=NF, 338-66-9; CsF, 13400-13-0; KF, 7789-23-3; NaF, 7681-49-4; LiF, 7789-24-4; C_3F_7NBrCl, 91523-61-4; $C_2F_5NBr_2$, 83696-32-6; C_2F_5NClBr, 91523-62-5; CF_3NBr_2, 88453-18-3; CF_3NCF_2NCl, 91523-63-6; CF_3NCF_2NH, 91523-64-7.

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N-Bromodifluoromethanimine

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The fascinating chemistry of the simple imines CF_2=NX (X = F, Cl) has provided routes to many novel fluorinated materials.[1-5] These compounds have also provided an opportunity to compare the reactivities of the carbon–nitrogen double bonds affected only by the halogen substituent on nitrogen and to compare the reactivities of the N–X bonds. Perfluoromethanimine is considerably more electrophilic than CF_2=NCl, but the N—X bond in the latter is considerably more reactive.

In the course of research with CF_2=NX (X = Cl, F), we became increasingly interested in preparing the N-bromo analogue. It was obvious that the latter would have the most reactive N–X bond and would represent an extremely useful synthon. However, all attempts to prepare it by methods analogous to the preparation of CF_2=NCl[6] and CF_2=NF[7] failed. We speculated that the fluoride-promoted oxidation of FC≡N by Br_2 might yield the desired compound. However, FC≡N is quite difficult to prepare,[8] and this reaction remained untried until an unexpected source of FC≡N became available. Pyrolysis of CF_3CF_2CF=NBr at 450

°C gives FC≡N and C_2F_5Br in excellent yield.[9] This provided the needed FC≡N, and our first attempt at the preparation of CF_2=NBr was successful.

$$FC≡N + MF \rightarrow F_2C=N^-M^+ \xrightarrow{\text{Br}_2}$$
$$F_2C=NBr + MBr \qquad M = K, Rb, Cs$$
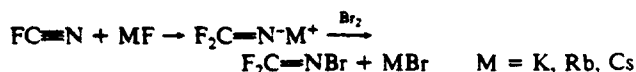
Some of the CF_2=NBr is further oxidized to CF_3NBr_2, which was previously prepared from the metal fluoride catalyzed conversion of CF_3NClBr to CF_3NBr_2 by Br_2.[4]

$$CF_2=NBr + MF \rightarrow CF_3NBr^-M^+ \xrightarrow{\text{Br}_2} CF_3NBr_2 + MBr$$

In a typical reaction, a 100-mL flask fitted with a glass–Teflon valve is charged with 15 mmol of active KF in a drybox.[10] The

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(10) Both CsF and RbF are effective in this reaction. However, KF appears to give higher yields. Metal fluorides are activated by fusing in a platinum crucible, followed by grinding to a fine powder in a ball mill under very anhydrous conditions. No reaction was observed with NaF.

Table I. Vibrational Assignments for CF$_2$=NX

	CF$_2$=NF[a]		CF$_2$=NCl		CF$_2$=NBr[c]	
	IR	Raman	IR[b]	Raman[c]	IR	Raman
C=N	1740.3 s	1733 m, p	1728 vs	1731 m, p	1742R vs[e] 1732P	1731 w, p
CF$_2$(as)	1385.5 s	1388 vw, p	1322 s	1322 vw, p	1305R vs[e] 1293P	1305 vw, p
NX	1021.2 s	1013 w, p	771 m	777 vs, p	726R m[e] 718P	727 s, p
CF$_2$(s)	932.9 s	932 vvs, p	981 s	989 m, p	981R 976Q s 972P	981 w, p
δ-CF$_2$	640	644 vs, p	598 w	598 s, p	578 w	587 m, p
ρ-CF$_2$	520.0 w	522 s, p	465 w	465 vs, p	391 w	390 vs, p
δ-NX	285.7 w	291 w, p	228 m[c,d]	237 m, p	200?[f]	199 m, p
β-CF$_2$	643.2 m	649 m, dp	658 m	659 m, dp	673R 665Q m 657P	663 w, dp
tors	302.5 w	306 m, dp	234 m[c,d]	245 sh, dp?	213 vw[g]	225 vs, dp?

[a] Reference 12. [b] Reference 11. [c] This work. IR taken on a Perkin-Elmer 1430 Data System using a 10-cm cell fitted with CsI windows. Raman spectra were taken on a Spex 1403 Ramalog Double Spectrometer with a Scamp data system. Samples were contained in a low-temperature liquid cell; excitation was by the 514.5 nm line of an argon ion laser (CF$_2$=NCl, 400 mW; CF$_2$=NBr, 100 mW). [d] Two overlapping bands. [e] Q branches clearly evident but not readily resolved. [f] Low-wavenumber limit of instrumentation was 200 cm^{-1}. Comparison of background and sample spectrum indicates presence of a medium absorption just below 200 cm^{-1}. [g] Presence of a weak band at 300 torr is clearly evident. At higher pressures, attack of CF$_2$=NBr on the CsI windows is rapid.

flask is then evacuated and cooled to -196 °C, and Br$_2$ (4.8 mmol) and FC≡N (3.5 mmol) are added by vacuum transfer. The reactor is then warmed to 22 °C in a water bath while agitating the contents by shaking. Reaction is rapid near 22 °C, and after 1 h, the volatile materials are pumped through a series of cold traps yielding (mmol) CF$_3$NBr$_2$ (-75 °C, 1.3) CF$_2$=NBr (-111 °C, 1.3), and small amounts of FC≡N and C$_2$F$_5$Br (-196 °C), the latter present as an impurity in the starting FC≡N.

N-Bromodifluoromethanimine is a pale yellow gas (bp 14.5 °C, log P(torr) = 6.5472 − (642.38/T) − (118655/T^2), ΔH_{vap} = 6.71 kcal/mol, ΔS_{vap} = 23.3 eu), which freezes to a pale yellow solid (mp -93 to -92 °C). A UV-vis spectrum (210–780 nm) of the gas at 5 torr (10 cm) exhibits an intense absorption at 240 nm (ϵ_{max} 651 M^{-1} cm^{-1}) with a weak shoulder near 340 nm. At 20 torr, absorption begins at 600 nm. Under the same conditions, CF$_2$=NCl shows evidence of strong absorption below 210 nm.

The mass spectrum of CF$_2$=NBr exhibits intense molecular ions in both EI (100%) and CI (100%) at 143/145 and 144/146, respectively. A vapor-density molecular weight determination gave a value of 144 (calcd 143.923). The ^{19}F NMR (1% in

![structure diagram]
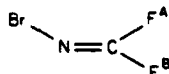
80:20:1/CCl$_4$:CDCl$_3$:CFCl$_3$) gave the expected AB spin system with A -31.3, B -54.3, and $^2J_{AB}$ = 68 Hz.

The infrared (g) and Raman (l) spectra allow a good assignment of the fundamental vibrational modes in CF$_2$=NBr based on C_s

symmetry. These assignments were easily made by comparison with the spectra of CF$_2$=NF and CF$_2$=NCl.[11,12] For CF$_2$=NCl, previous assignments based on only a partial infrared spectrum must be revised in view of Raman data obtained in this work. The assignments for the compounds are compared in Table I by using the description previously given for CF$_2$=NF.[12] Within the resolution limit of our instrument, the band contours for CF$_2$=NBr appear to be nearly identical with those of CF$_2$=NF. For both CF$_2$=NBr and CF$_2$=NCl, the assignment of the torsional frequency is tentative. Neither molecule exhibits a distinct Raman band for this mode. However, very weak features at a somewhat higher frequency than δ-NX are evident in the spectra. In the case of CF$_2$=NF, the torsion is the second least intense Raman band, and this provides support for the assignments in CF$_2$=NCl and CF$_2$=NBr. Taken together, the assignments in Table I provide very reasonable values for the three compounds.

The chemistry of CF$_2$=NBr is under active investigation and will be reported separately. Other reactions of FC≡N suggested by this work are also being explored.

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Some Reactions of (Fluoroimido)tetrafluorosulfur[1]

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(Fluoroimido)tetrafluorosulfur undergoes a number of reactions with strong electrophiles, involving addition to the sulfur–nitrogen double bond. It also reacts readily with fluoride ion, forming the reactive nucleophile SF_5NF^-. Chlorine(I) fluorosulfate, bromine(I) fluorosulfate, and peroxydisulfuryl difluoride add to $F_4S=NF$, forming the respective cis adducts. The ^{19}F NMR spectra of these adducts provide the first examples of magnetic nonequivalence induced in an octahedral system by an adjacent chiral center. The anion SF_5NF^-, generated in situ from $F_4S=NF$ and KF, reacts readily with Br_2, forming SF_5NBrF, and with acyl fluorides, forming $RCONFSF_5$. The SF_5NF^- ion also reacts with $F_2C=NF$ to form $(SF_5NF)FC=NF$, which is isomerized to the unusual azo compound $F_5SN=NCF_3$ in the presence of CsF. Self-reaction of $F_4S=NF$ in the presence of KF does not produce the expected dimer $(SF_5NF)F_3S=NF$. Instead, extensive decomposition is observed, along with a low yield of the unusual amine $(SF_5)_2NF$.

Introduction

Compounds of sulfur, nitrogen, and fluorine containing multiple N–S bonds are well-known and have led to much unique and interesting chemistry. Among these compounds are examples containing triple (e.g., $N\equiv SF$, $N\equiv SF_3$, and $N\equiv SF_2(CH_3)$) and double (e.g., $F_4S=NR$, $(R)F_3S=NR$, $XX'F_2S=NR$, $XX'S(=NR)_2$, $O_2S=NR$, and $(O)F_2S=NR$) bonds.[2] Despite the long and chemically productive history of this general class of compounds, reports of the synthesis and chemistry of imidotetrafluorosulfur compounds, $F_4S=NR$,

have been few. Among the compounds of this class so far reported are $F_4S=NCF_3$,[3] $F_4S=NCH_3$,[4] and $F_4S=NSF_5$;[5] of these three compounds, extensive chemical investigations have been reported only for $F_4S=NSF_5$.[5] Some chemistry of a (perfluoroalkyl)(trifluoroimido)sulfur compound, $(CF_3)F_3S=NCF_3$,[6] has also been reported.

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Recently, the synthesis and characterization of the simplest fluorinated member of the series, $F_4S=NF$, (fluoroimido)tetrafluorosulfur, was reported.[7] Herein we wish to describe an investigation of some of the chemistry of this compound. (Fluoroimido)tetrafluorosulfur has been found to undergo reactions with acyl fluorides, perfluoromethanimine, bromine, and chlorine in the presence of KF. In addition, reaction of $F_4S=NF$ with $F_2C=NF$ in the presence of CsF leads to the azo compound $F_5SN=NCF_3$. These reactions are believed to proceed by way of the anion SF_5NF^-, formed by the reaction of $F_4S=NF$ with F^-. Ample precedent for the formation of SF_5NF^- may be found in mechanistically similar chemistry reported for $F_2C=NCF_3$,[8] $F_4S=NSF_5$,[5] $F_4S=O$,[9] and $F_2C=NF$.[10]

In another type of reaction, the strong electrophiles $XOSO_2F$ ($X = Br, Cl, OSO_2F$) have been found to add directly to the double bond of $F_4S=NF$, forming the unusual octahedral sulfur(VI) compounds cis-$SF_4(OSO_2F)NFX$. While many cis-disubstituted X_2SF_4 compounds have been reported,[11] in only a few instances have the two non-fluorine substituents been different. Specific examples of such compounds include $SF_4(OCF_3)OOCF_3$,[11b] $SF_4(NF_2)OCF_3$,[11c] $SF_4(Cl)-OSO_2CF_3$,[11d] and $SF_4(Cl)OSO_2F$.[11e] In each of these specific cases, the reported ^{19}F NMR spectra have been complex, because the low symmetry of the molecules, due to the difference in the two substituents, increased the number of magnetically nonequivalent types of fluorine from two to three. In the new examples of cis-disubstituted $XX'SF_4$ compounds which we report here, an additional factor is present: the chirality of the NFX substituent. The proximity of this group to three of the four central fluorine atoms allows all four central fluorine atoms to become magnetically nonequivalent, giving rise to complex and highly characteristic ^{19}F NMR spectra.

Experimental Section

General Procedures. Volatile compounds were handled in either a stainless steel or a glass vacuum system fitted respectively with Teflon-packed stainless steel valves or with glass–Teflon valves.

Pressures in the glass system were measured with a Wallace and Tiernan Series 1500 differential pressure gauge; those in the metal system were measured with a precision Heise Bourdon tube gauge. Temperatures were measured with a digital indicating iron–constantan thermocouple. Amounts of reactants and products were measured either by direct weighing or by PVT measurements, assuming ideal gas behavior.

Infrared spectra were recorded with a Perkin-Elmer Model 1330 spectrometer. A 10-cm glass cell fitted with AgCl windows was used. ^{19}F NMR spectra were recorded with a Varian XL-100-15 spectrometer, using ~80 mol % CFCl$_3$ as solvent and internal reference. High-field chemical shifts are negative. Mass spectra were obtained with a Finnigan 4021-C instrument at 70 eV for EI and CI (CH$_4$). Samples were introduced by direct gas injection.

Melting points were determined by a modified Stock procedure. Vapor pressures as a function of temperature were determined by the method of Kellogg and Cady[12] or by the use of a small isoteniscope.[13] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purification of reaction products, chromatography was carried out on a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. A 10 ft × $^3/_8$ in. or 2 ft × $^3/_8$ in. column packed with 35% halocarbon 11-21 polymer oil on acid-washed Chromasorb P was used.

Reagents. Chlorine, CF$_3$COF, CH$_3$COF, and C$_2$H$_4$ were obtained from commercial sources and were used as received. Active KF, CsF, RbF, and NaF–KF eutectic mixture[14] were prepared by fusion in a Pt dish, followed by grinding to fine powders in a dry mortar inside of a drybox. Carbonyl fluoride was prepared from COCl$_2$ and NaF in CH$_3$CN at 40 °C.[16] Perfluoropropionyl fluoride was prepared from the reaction of CF$_3$CF$_2$COCl with SbF$_3$/Cl$_2$. Bromine and CFCl$_3$ were dried by storage over P$_4$O$_{10}$.

((Fluorocarbonyl)imido)sulfur difluoride was prepared by a literature method,[15] except for the heating step, which was omitted. This modification led to the product in higher yield and in greater purity than were reported in ref 15. (Fluoroimido)tetrafluorosulfur was prepared as described previously,[7] with two exceptions: the $F_2S=NCOF$ was prepared as just described, and the dehydrofluorination of SF$_5$NHF to give $F_4S=NF$ was done with a NaF–KF eutectic (55% NaF by weight) mixture[14] rather than with KF. Reaction times, at −4 °C, varied from 15 min to ~5 h, depending on how many times the NaF–KF had been used previously. *Caution: On two occasions ~3-mmol samples of $F_4S=NF$ exploded with considerable force while they were warmed from −196 to +22 °C in a glass vessel. Due caution must be exercised in handling this compound and its derivatives, and sample size should be limited to 3 mmol.*

Peroxydisulfuryl difluoride,[17] ClOSO$_2$F,[18] BrOSO$_2$F,[19] and $F_2C=NF$[20] were prepared according to literature methods.

General Procedure for Reactions Involving Alkali-Metal Fluorides. Inside a drybox, the fused, finely powdered metal fluoride was placed in a one-piece ca. 120-mL Pyrex flask fitted with a glass–Teflon valve and containing a Teflon-coated magnetic stirring bar. After removal from the drybox and evacuation of the flask, the volatile reactant(s) were condensed into the flask at −196 °C, and the metal fluoride was stirred for an appropriate length of time at ca. 23 °C.

At the end of the reaction period, the volatile materials were separated by passage through a series of traps maintained at appropriate temperatures. Further purification by GLC was done in some cases.

Preparation of SF$_5$N(F)COF. Carbonyl fluoride (6.0 mmol) and $F_4S=NF$ (1.5 mmol) were condensed into a flask containing fused, powdered KF (1.36 g, 23.4 mmol), and the KF was stirred for 3 h at 23 °C. Fractionation (−111 and −196 °C) of the volatile materials

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by pumping on the sample container as it was warmed from −196 °C to the ambient temperature gave essentially pure SF$_5$N(F)COF (1.4 mmol, 93% yield) in the −111 °C trap. The material was freed of minor impurities by GLC.

F^{A}SF$^B_4$NF^{X}COF^M: bp 29 °C; mp −130 to −129 °C; mol wt 207.05 (calcd), 203.4 (found); log P (torr) = 5.939 − 410.2/T − 156 439.7/T^2; ΔH_{vap} = 6.60 kcal/mol; ΔS_{vap} = 21.8 eu; IR 1925 (sh, w), 1875 (C═O, s), 1810 (sh, w), 1250 (m), 1215 (m), 1070 (m), 1000 (m), 920 (s), 855 (s), 745 (w), 715 (w), 685 (m), 605 (s), 540 (sh, w); MS (CI) major m/z (%) 209 (1.4), 208 (MH$^+$, 100.0), 188 (MH$^+$ − HF, 5.8), 142 (SF$_5$NH$^+$, 1.2), 127 (SF$_5$$^+$, 31.8), 105 (HNSF$_3$$^+$, 1.2), 89 (SF$_3$$^+$, 15.4), 82 (4.5); MS (EI) major m/z (%) 129 (4.0), 127 (SF$_5$$^+$, 100.0), 108 (SF$_4$$^+$, 5.2), 91 (2.0), 89 (SF$_3$$^+$, 55.4), 85 (11.4), 70 (SF$_2$$^+$, 10.9), 69 (1.1), 51 (SF$^+$, 5.7), 47 (43.2), 46 (3.7), 44 (42.7), 42 (2.2); NMR A δ 58.4 or 57.7 (complex overlaps B), B 62.0 (complex), M −6.1 (d quintets), X −38.7 (br d) ($J_{AB} \simeq$ 150 Hz, J_{BM} = 14.0 Hz, J_{MX} = 60.0 Hz).

Preparation of SF$_5$N(F)COCF$_3$. Trifluoroacetyl fluoride (12.5 mmol) and F$_4$S═NF (2.5 mmol) were condensed into a flask containing fused, powdered KF (1.36 g, 23.4 mmol), and the mixture was stirred for 20 h at ca. 23 °C. Fractionation (−85 and −196 °C, while the sample container was warmed from −196 °C) gave essentially pure SF$_5$N(F)COCF$_3$ (1.3 mmol, 52% yield) in the −85 °C trap. Some noncondensable gas was formed in this reaction. The product was freed of minor impurities by GLC.

F^{A}SF$^B_4$N(F^M)COCF$^X_3$: bp 51 °C; log P (torr) = 6.490 − 724.4/T − 144 132.5/T^2; ΔH_{vap} = 7.39 kcal/mol; ΔS_{vap} = 22.8 eu; IR 1790 (s), 1750 (w, sh), 1315 (m), 1240 (s), 1190 (s), 1070 (s), 975 (w), 920 (s), 875 (s), 850 (sh), 815 (m), 730 (w), 695 (s), 645 (w), 605 (s), 585 (m), 525 (m) cm^{-1}; NMR A δ 58.0 (m), B 61.5 (m), M −53.7 (br s), X −73.4 (d), ($J_{AB} \simeq$ 150 Hz, $J_{AM} \simeq$ 0, J_{BM} = ?, J_{MX} = 22 Hz); MS (EI) major m/z (%) 141 (4.1), 127 (58.1, SF$_5$$^+$), 96 (25.6), 88 (47.7), 69 (100.0, CF$_3$$^+$); MS (CI) major m/z (%) 258 (100.0, MH$^+$), 162 (15.4, SF$_5$NHF$^+$), 142 (22.4); 127 (87.2, SF$_5$$^+$), 114 (17.2), 88 (41.7), 69 (29.1, CF$_3$$^+$).

Preparation of SF$_5$N(F)COCF$_2$CF$_3$. Perfluoropropionyl fluoride (8.0 mmol) and F$_4$S═NF (1.9 mmol) were condensed into a flask containing fused, powdered KF (1.36 g, 23.4 mmol), and the mixture was stirred for ca. 7 h at ca. 23 °C. Fractionation (−78 and −196 °C, while the sample container was warmed from −196 °C) gave essentially pure SF$_5$N(F)COCF$_2$CF$_3$ (0.72 mmol, 38% yield) in the −78 °C trap. Some noncondensable gas was observed in this reaction. The product was freed of trace impurities by GLC.

The use of only a fourfold excess of CF$_3$CF$_2$COF, relative to F$_4$S═NF, led to low yields (8–10%) of the product.

F^{A}SF$^B_4$NF^{M}COCF$^X_2$CF$^Y_3$: mp −60.4 to −59.8 °C; IR 1775 (s), 1485 (w), 1350 (m), 1330 (m), 1275 (s), 1225 (s), 1205 (s), 1170 (s), 1120 (w), 1095 (m), 1020 (s), 925 (s), 870 (s), 830 (w), 785 (m), 740 (m), 690 (s), 605 (s), 585 (s), 565 (m), 535 (m) cm^{-1}; NMR A δ 57.8 (m), B 63.7 (m), M −52.8 (br s), X −119.6 (d-q), Y −82.3 (d-t) ($J_{AB} \simeq$ 150 Hz, $J_{XY} \simeq$ 1 Hz, J_{MX} = 33 Hz, J_{MY} = 8.0 Hz); MS (EI) major m/e (%) 147 (29.1, C$_2$F$_5$CO$^+$), 141 (3.2, SF$_5$N$^+$), 127 (90.5, SF$_5$$^+$), 119 (83.7), 108 (3.9), 100 (9.1), 89 (47.5, SF$_3$$^+$), 85 (11.6), 70 (12.2), 69 (100.0, CF$_3$$^+$), 50 (11.6, CF$_2$$^+$), 47 (19.5); MS (CI) major m/z (%) 308 (82.7, MH$^+$), 290 (5.8), 250 (5.9), 182 (12.6), 164 (14.0), 147 (19.5, C$_2$F$_5$CO$^+$), 142 (14.7, SF$_5$NH$^+$), 127 (78.71, SF$_5$$^+$), 119 (14.3), 104 (8.1), 89 (100.0, SF$_3$$^+$).

Preparation of SF$_5$N(F)C(O)NSF$_2$ ((Fluorocarbonyl)imido)sulfur difluoride (1.0 mmol) and F$_4$S═NF (0.5 mmol) were condensed into a flask containing fused, powdered KF (0.65 g, 11 mmol), and stirring was begun. At the end of each of four successive ca. 20-min intervals, the volatile materials were fractionated (−40 and −195 °C), allowing removal of some of the product (−40 °C trap) before it could decompose completely. The materials from the −195 °C trap were then returned to the flask for further reaction. After the last cycle, a total of 0.0311 g (0.114 mmol, 22% yield) of product had been collected, the −195 °C trap as shown by IR to contain F$_2$S═NCOF and SF$_5$N(F)COF.

F^{A}SF$^B_4$NF^{X}CONSF$^M_2$: colorless liquid at 23 °C; IR 1770 (s), 1435 (w), 1345 (sh), 1315 (s), 1255 (w), 1190 (w), 1185 (m), 1065 (w), 1015 (m), 915 (s), 885 (m), 850 (s), 765 (s), 750 (sh), 725 (s), 705 (sh), 605 (s), 555 (w), 485 (m) cm^{-1}; NMR A most intense peak δ 62.1 (m, partly overlaps B), B 62.6 (m), M 46.9 (br s), X −37.5 (br s), small impurity peaks 53.6 (s) and 52.1 (s); MS (EI) major m/z (%) 188 (3.0, SF$_5$NFCO$^+$), 129 (2.3), 127 (50.6, SF$_5$$^+$), 114 (4.8), 112 (100.0, F$_2$SNCO$^+$), 108 (2.3), 85 (12.7), 84 (4.4), 80 (2.0), 72

(2.3), 70 (50.6), 69 (9.0), 66 (2.5), 65 (12.2), 64 (20.1), 61 (2.5), 51 (13.2); MS (CI) major m/z (%) 273 (100.0, MH$^+$), 253 (3.4), 188 (2.2, SF$_5$NFCO$^+$), 162 (9.2), 142 (8.1), 132 (5.9), 127 (8.1, SF$_5$$^+$), 114 (4.4), 113 (2.0), 112 (72.0, F$_2$SNCO$^+$), 104 (3.0).

Attempted KF-Catalyzed Reactions of F$_4$S═NF with SF$_5$N(F)COF and with CH$_3$COF. When these reactions were attempted, under conditions similar to those just described, the F$_4$S═NF was destroyed and the acyl fluorides were recovered unchanged.

KF-Catalyzed Self-Reaction of F$_4$S═NF. (Fluoroimido)tetrafluorosulfur (1.5 mmol) was condensed into a flask containing fused, powdered KF (5.57 g, 95.9 mmol), and the KF was stirred for ~20 h at ~23 °C. Fractionation (−78, −110, −196 °C) of the volatile materials gave crude (SF$_5$)$_2$NF (0.17 mmol, ~23% conversion of F$_4$S═NF) in the −78 °C trap. The other traps contained mainly SF$_4$, SOF$_2$, SiF$_4$, and SF$_6$; noncondensable gas was also formed.

(SF$_5$)$_2$NF was purified by GLC. The ^{19}F NMR, mass, and IR spectra of the material showed good agreement with those reported in ref 5.

Preparation of SF$_5$N(F)CF═NF. Unless purified by GLC, the F$_2$C═NF prepared according to ref 20 usually contains CF$_3$COF as an impurity. This appears not to interfere significantly, since F$_2$C═NF seems to be by far the more reactive of the two substances.

Perfluoromethanimine (1.6 mmol; containing some CF$_3$COF) and F$_4$S═NF (1.7 mmol) were condensed into a flask containing fused, powdered KF, and the mixture was stirred for 135 min. Fractionation (−111 and −196 °C, while the sample container was warmed from −196 °C) of the volatile materials gave crude (containing, by IR, some CF$_3$COF) SF$_5$N(F)CF═NF in the −111 °C trap. After further purification by GLC, 0.83 mmol (~50% yield) of SF$_5$N(F)CF═NF was obtained.

In another, larger scale, GLC purification of SF$_5$N(F)CF═NF, a very minor component of high retention time was noted. Its infrared and mass spectra indicated that its structure was [SF$_5$N(F)][CF$_3$N-(F)]C═NF.

F^{A}SF$^B_4$NF^{M}CF^X═NF^N: colorless glass, flows at −141 °C; IR 1670 (s, C═N), 1300 (s), 1060 (w), 1010 (m), 980 (s), 915 (s), 870 (s), 780 (m), 745 (w), 705 (w), 685 (m), 605 (s), 580 (m) cm^{-1}; MS (CI) m/z (%) 253 (2.0), 227 (4.5), 226 (1.4), 225 (MH$^+$, 83.0), 207 (1.2), 205 (MH$^+$ − HF, 9.9), 187 (1.2), 149 (2.4), 129 (4.5), 127 (SF$_5$$^+$, 100.0), 111 (2.1), 107 (4.1), 99 (2.5), 91 (1.9), 89 (SF$_3$$^+$, 42.8), 87 (1.8), 80 (1.03), 79 (40.4), 62 (5.1); (EI) m/z (%) 129 (4.4), 127 (SF$_5$$^+$, 100.0), 108 (SF$_4$$^+$, 4.4), 97 (19.9), 89 (SF$_3$$^+$, 71.9), 86 (1.1), 85 (21.5), 83 (1.2), 70 (SF$_2$$^+$, 19.2), 69 (1.3), 64 (11.5), 59 (6.0), 51 (7.4), 50 (4.0), 47 (1.6), 46 (3.7), 45 (4.4), 40 (3.4); NMR A complex most intense peak δ 56.8, B complex most intense peak 57.2, M −30.6 (br d), N −11.0 (br s), X −70.2 (br m) (J_{MX} = 16 Hz, other coupling constants not readily determined). (SF$_4$NF)(CF$_3$NF)C═NF: yellowish glass at −196 °C; IR 1670 (w, C═N), 1600 (w), 1490 (w), 1295 (s, sh), 1250 (s), 1195 (s), 1125 (m), 1020 (m), 975 (m, sh), 920 (s), 875 (m), 845 (m), 800 (w), 780 (m), 695 (m), 605 (m), 575 (m), cm^{-1}; MS (CI) m/z (%) 308 (MH$^+$, 9.1), 288 (MH$^+$ − HF, 3.4), 247 (4.4), 225 (MH$^+$ − HF, 9.0), 210 (10.0), 208 (1.1), 192 (4.8), 162 (2.6), 152 (1.7), 151 (1.0), 149 (MH$^+$ − SF$_5$N, 21.7), 147 (3.6), 144 (1.0), 143 (7.5), 142 (SF$_5$NH$^+$, 14.5), 135 (1.5), 129 (4.9), 127 (SF$_5$$^+$, 53.9), 124 (3.1), 122 (SF$_4$N$^+$, 15.6), 114 (1.0), 109 (1.7), 107 (1.3), 105 (1.3), 104 (4.5), 103 (1.1), 102 (1.3), 101 (6.4), 99 (1.5), 89 (SF$_3$$^+$, 65.7), 87 (4.0), 85 (3.1), 84 (4.8), 79 (6.6), 74 (2.1), 70 (1.7), 69 (CF$_3$$^+$, 100.0), 67 (8.9), 66 (3.1), 65 (5.2), 62 (3.3); MS (EI) m/z (%) 149 (1.4), 137 (1.1), 135 (4.0), 129 (2.7), 127 (SF$_5$$^+$, 62.2), 119 (2.4), 114 (2.4), 108 (SF$_4$$^+$, 1.9), 100 (3.4), 97 (1.1), 92 (1.1), 91 (1.5), 89 (SF$_3$$^+$, 35.7), 87 (4.0), 86 (1.0), 85 (25.6), 83 (17.1), 76 (1.1), 70 (SF$_2$$^+$, 13.5), 69 (CF$_3$$^+$, 100.0), 67 (4.2), 66 (3.4), 65 (1.2), 64 (8.4), 59 (4.1), 54 (2.6), 51 (5.7), 50 (CF$_2$$^+$, 21.9), 48 (6.5), 47 (17.6), 46 (4.2), 45 (2.7), 44 (3.5), 43 (2.0), 40 (1.4).

Preparation of F$_5$SN═NCF$_3$. Perfluoromethanimine (1.4 mmol) and F$_4$S═NF (1.4 mmol) were condensed into a flask containing fused, powdered CsF (3.20 g, 21.0 mmol), and the CsF was stirred at ca. 23 °C for 45 min. Trap-to-trap fractionation (−119, −196 °C) of the volatile materials gave F$_5$SN═NCF$_3$ (1.0 mmol, 71% yield) in the −119 °C trap. The material was freed of minor impurities by GLC.

F^{A}SF$^B_4$N═NCF$^X_3$: very pale yellow liquid, bp 16 °C; mp −124.3 to −123.8 °C; mol wt 224.06 (calcd) 221 (found); log P (torr) = 8.112 − 1534.0/T + 5874.5/T^2; ΔH_{vap} = 6.83 kcal/mol; ΔS_{vap} = 23.6 eu; IR 1600 (m, −N═N−), 1245 (s), 1190 (s), 1160 (sh), 890 (s), 875 (w), 825 (w), 785 (w), 610 (m), 580 (m), 565 (sh) cm^{-1}; MS (CI) m/z (%) 225 (MH$^+$, 7.2), 127 (SF$_5$$^+$, 2.4), 104 (HNSF$_3$$^+$, 5.0), 91

(1.9), 89 (SF$_3$$^+$, 41.5), 77 (1.4), 70 (SF$_2$$^+$, 2.7), 69 (CF$_3$$^+$, 100.0), 67 (5.3); MS (EI) m/z (%) 127 (SF$_5$$^+$, 17.3), 108 (SF$_4$$^+$, 2.0), 91 (1.6), 89 (SF$_3$$^+$, 38.4), 86 (1.1), 70 (SF$_2$$^+$, 11.7), 69 (CF$_3$$^+$, 100.0), 64 (1.0), 51 (6.6), 50 (CF$_2$$^+$, 25.5), 48 (1.1), 47 (2.2), 46 (2.9), 44 (4.8); NMR A δ 56.0 (m), B 38.5 (m), X −71.6 (s) ($J_{AB} \simeq$ 150 Hz).

Isomerization of SF$_5$N(F)CF=NF. Exposure of SF$_5$N(F)CF=NF (0.31 mmol) to stirred, fused, powdered CsF (0.67 g, 4.4 mmol) for 25 min yielded F$_5$SN=NCF$_3$ quantitatively.

A similar experiment with fused, powdered RbF (0.42 g, 4.0 mmol) and SF$_5$N(F)CF=NF (0.46 mmol) for ca. 19 h, with periodic checking by IR, produced only a small amount of isomerization, with F$_5$S-N=NCF$_3$ being the only observable product.

Preparation of SF$_5$NBrF and SF$_5$NClF. (Fluoroimido)tetrafluorosulfur (0.50 mmol) and bromine (0.50 mmol) were condensed into a flask containing fused, powdered KF (5.6 g, 96 mmol), and the KF was stirred for ∼3 h at ∼25 °C. Fractionation of the volatile materials through −85, −126, and −196 °C traps gave SF$_5$NBrF, somewhat contaminated with Br$_2$, in the −85 °C trap, with the a smaller amount being collected at −126 °C. Some noncondensable gas was formed, and no F$_4$S=NF remained. The crude yield of SF$_5$NBrF was 80%.

In a similar manner, SF$_5$NClF^7 was prepared, in 48% yield, from F$_4$S=NF, Cl$_2$, and KF.

It was found that the Br$_2$ could be removed from the product by brief exposure to an excess of ethylene, followed by fractionation (−50, −85, −196 °C traps). 1,2-Dibromoethane was collected at −50 °C, while SF$_5$NBrF was collected at −85 °C.

F^{A}SF^B$_4$NBrF^X: mol wt 239.96 (calcd), 236 (found); IR 920 (vs), 860 (s), 780 (w), 725 (m), 690 (m), 600 (s), 580 (sh); NMR A δ 52.4 (m), B 47.1 (m), X 46.1 (br s) (J_{AB} = 145 Hz, other coupling constants not readily determined).

Reaction of F$_4$S=NF with ClOSO$_2$F. Chlorine(I) fluorosulfate (1.6 mmol) was transferred through a short glass connection, and under static vacuum, to an FEP tube (ca. 20-mL volume) equipped with a stainless steel valve and held at −196 °C. (Fluoroimido)tetrafluorosulfur (1.7 mmol) was then condensed into the reactor (in some places on the walls of the vessel, a brief flash of brown-red color was seen). The reactor was then placed in a −30 °C bath. The reaction mixture was held at −30 °C for 10 min and then warmed to room temperature. Trap-to-trap fractionation (−40, −196 °C) of the resulting light yellow liquid gave 0.35 mmol of colorless liquid, which was shown by NMR (see Results and Discussion) to consist of a 65:15:20 mixture of cis-SF$_4$(OSO$_2$F)FCl, cis-SF$_4$(OSO$_2$F)$_2$, and trans-SF$_4$(OSO$_2$F)$_2$. cis-SF$_4$(OSO$_2$F)NFCl appeared to be thermally unstable near 24 °C, decomposing with moderate rapidity, with concomitant formation of a yellow gas, presumably Cl$_2$.

Preparation of cis-SF$_4$(OSO$_2$F)NFBr. Bromine(I) fluorosulfate (0.6 mmol) was transferred through a short glass connection, under static vacuum, to a ca. 120-mL glass reactor held at −196 °C. All parts of the system were treated with the equilibrium vapor of BrOSO$_2$F before the transfer was made. The transferred BrOSO$_2$F was then allowed to melt and distributed as a thin film in the flask. The film was then frozen at −196 °C, and F$_4$S=NF (0.6 mmol) was condensed into the flask. The flask was then placed in an ethanol bath in a Dewar flask, at −100 °C, and left to gradually warm. The contents of the flask showed marked discoloration by the time the temperature reached −90 °C. After 6.5 h, the temperature had reached −45 °C, and the flask contents had become dark brown-violet, for the most part. Further warming, in the air, caused disappearance of this color. The colorless liquid that formed began to decompose fairly rapidly at room temperature, with concomitant formation of a brown-orange vapor (presumably Br$_2$). Trap-to-trap fractionation (−30, −196 °C) gave a colorless liquid in the −30 °C trap. This material released Br$_2$ when handled in the vacuum system and appeared to have an equilibrium vapor pressure of ca. 5 torr. An NMR sample was prepared by transfer of the material, under static vacuum, through a short glass connection, to an NMR tube maintained at −196 °C. The sample was then warmed to ca. −30 °C, and volatile impurities were pumped away over 30 min. Fluorotrichloromethane was then added at −196 °C. See Results and Discussion for details of the NMR spectrum.

Preparation of cis-SF$_4$(OSO$_2$F)NF(OSO$_2$F). Peroxydisulfuryl difluoride (1.0 mmol) and F$_4$S=NF (1.0 mmol) were condensed into a ca. 120-mL Pyrex flask equipped with a glass–Teflon valve and held at −196 °C. The flask was then left to warm in the air (∼23 °C). (*Caution*: More rapid warming, with use of a water bath, once resulted

in a minor explosion.) The reaction mixture was then left at ∼23 °C for 1.5 h. Fractionation (−40, −80, −196 °C) gave 0.24 g (0.71 mmol, 71% yield) of cis-SF$_4$(OSO$_2$F)NF(OSO$_2$F) in the −40 °C trap. Some noncondensable gas was present, and a small amount of FSO$_2$OOSO$_2$F collected in the −80 °C trap. The −196 °C trap contained (by IR) mostly (FSO$_2$)$_2$O. Some FSO$_2$OOSO$_2$F and SiF$_4$ were also present.

cis-SF$_4$(OSO$_2$F)NF(OSO$_2$F): colorless glass at −196 °C; equilibrium vapor pressure at 23 °C 6 torr; IR 1490 (s, OSO$_2$F), 1250 (s, OSO$_2$F), 1025 (w), 990 (m), 925 (s), 890 (s), 870 (s), 810 (s), 745 (w), 695 (m), 680 (m), 650 (w), 615 (sh, w), 580 (s), 550 (s), 455 (w). See Results and Discussion for details of the NMR spectrum.
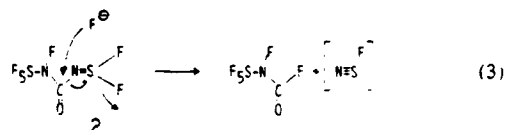
Results and Discussion

Fluoride-Catalyzed Reactions of F$_4$S=NF with Acyl Fluorides. The reactions of certain acyl fluorides with F$_4$S=NF in the presence of KF lead to acylated amidopentafluorosulfur derivatives, SF$_5$N(F)COR. The formation of these products is best explained by invoking the ion SF$_5$NF$^-$, formed from F$_4$S=NF and F$^-$, as an intermediate. Acylation of this ion would lead to the observed products. These processes are illustrated in eq 1 and 2. The yield of acylated

$$F_4S=NF + F^- \rightarrow F_5S-NF^- \quad (1)$$
$$\mathbf{1}$$

$$F_5S-NF^- + RCOF \rightarrow F_5S-N(F)COR + F^- \quad (2)$$

product is markedly dependent on the nature of the R group. Increasing the size of R or decreasing its electronegativity led to drastic decreases in the yields of products. Thus, a yield of ∼90% was obtained for R = F; changing R to CF$_3$ or CF$_3$CF$_2$, under similar conditions, led to yields of acylated products of 53% and 8%, respectively. (The yield of SF$_5$N(F)COCF$_2$CF$_3$ could be increased, however, by using a large excess of CF$_3$CF$_2$COF.) No acylated product was obtained when R was CH$_3$ or SF$_5$NF. Also, since F$_4$S=NF readily decomposes in the presence of active KF, there is, in all of these reactions, a competition between destruction of F$_4$S=NF and acylation of the anion derived from it, leading to low yields of acylated products when the less reactive acyl fluorides are used.

In the case where R = F$_2$S=NCO, a third process was found to be operating, namely, catalytic destruction of the acylated product by KF. This process is illustrated in reaction 3. The acyl fluoride F$_2$S=NCOF is known to decompose in

$$(3)$$

an analogous manner in the presence of CsF,^{15} so the observed destruction of SF$_5$N(F)CONSF$_2$ by active KF is not particularly surprising. A 22% yield of 2 was obtained by fractionation of the reaction mixture at short intervals; this procedure removed a substantial amount of 2 before it could react further.

The pentafluoro(fluoroamido)sulfur compounds are all stable, volatile, colorless liquids at room temperature. They were characterized by their mass, infrared, and ^{19}F NMR spectra and by their physical properties.

Oxidation of SF$_5$NF$^-$ by Br$_2$ and Cl$_2$. The ion SF$_5$NF$^-$, generated from F$_4$S=NF and KF, was found to react readily with Br$_2$ or Cl$_2$, forming respectively SF$_5$NBrF (4) and SF$_5$NClF (5) as illustrated in eq 4. This behavior is analogous

$$(4)$$

$$X = Br \ (4), Cl \ (5)$$

to that reported for the ion CF_3NF^-.[10] Compound 5 has been reported previously,[7] but this constitutes the first synthesis of SF_5NBrF.

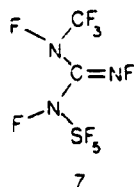Compound 4 is a pale greenish yellow liquid that is only moderately stable at room temperature. It can be handled in a glass vacuum system for short periods, but it appears to be photosensitive, decomposing upon extensive handling, with release of Br_2, as evidenced by the color that develops.

Fluoride-Catalyzed Reactions of F_4S=NF with F_2C=NF. Perfluoromethanimine was found to undergo a facile reaction with SF_5NF^- (generated from F_4S=NF and KF), leading to compound 6. Compound 6, a stable, colorless liquid, was

$$F_5S-N\overset{F}{\underset{\cdot\cdot}{}} + F_2C=NF - - - \rightarrow F_5S-N\overset{F}{\underset{F}{}}\overset{}{\underset{C}{}}-NF \quad \overset{F^-}{} \quad (5)$$
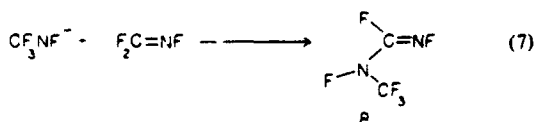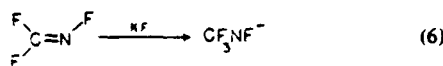
characterized by its IR, ^{19}F NMR, and mass spectra. In addition to 6, a very small amount of a heavier product was isolated. Infrared and mass spectral evidence suggested that its structure is 7, but further characterization was precluded
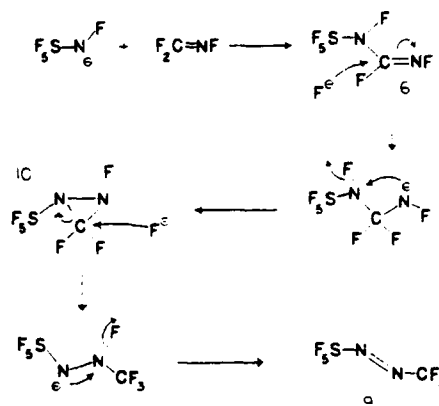
$$\overset{F}{\underset{F}{}}N\overset{CF_3}{\underset{}{}}C=NF\overset{}{\underset{}{}}N\overset{}{\underset{SF_5}{}}$$

7

by the small amount of material. An ion at m/z 308 (2.1%), corresponding to MH$^+$, was observed in the chemical ionization mass spectrum, with no heavier ions of significant intensity being detected. Ions of high relative abundance were also detected at m/z 127 (SF_5^+, 53.9%) and 69 (CF_3^+, 100.0%). The infrared spectrum of the material, in addition to major absorptions attributable to C–F stretching vibrations and S(VI)–F vibrations, contained a band at 1670 cm^{-1} attributable to a C=N stretch. Compound 7 could arise by nucleophilic attack of CF_3NF^- (from F_2C=NF + F$^-$) on the primary product 6. The lack of reactivity of 6 with SF_5NF^- is not unexpected, since the structurally similar $SF_5N(F)COF$ was also unreactive. Presumably the smaller CF_3NF^- is, for steric reasons, better able to attack 6. An alternative explanation for the formation of 7 is attack by SF_5NF^- on $(CF_3NF)F$-C=NF (8) (see below).

It was interesting to find that no important competing reactions occurred in this system. For instance, self-reaction of F_2C=NF over active KF leads smoothly to the formation of a dimer,[10] as illustrated in eq 6 and 7. There was no indication

$$\overset{F}{\underset{F}{}}C=N\overset{F}{\underset{}{}} \overset{KF}{\longrightarrow} CF_3NF^- \quad (6)$$

$$CF_3NF^- + F_2C=NF \longrightarrow \overset{F}{\underset{F}{}}N\overset{}{\underset{CF_3}{}}C=NF \quad (7)$$
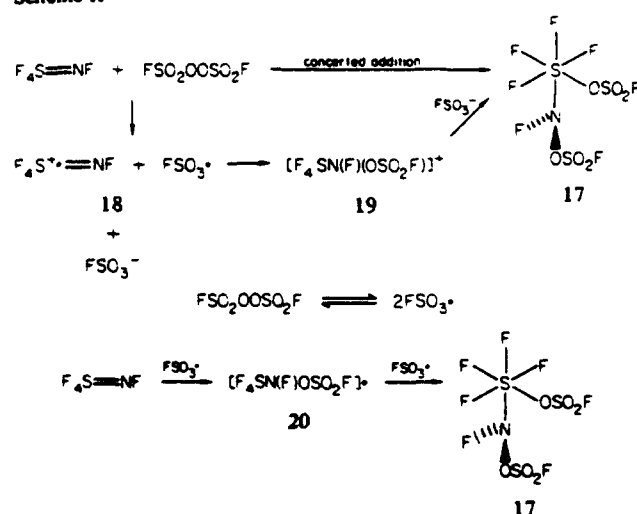
8

that this process was occurring efficiently, even though CF_3NF^- must have been present. The results of the experiment may be rationalized in either of two ways: (1) SF_5NF^- is, in the absence of overriding steric factors, a much more reactive nucleophile than CF_3NF^-, being rapidly trapped by either F_2C=NF (leading to 6) or $(CF_3NF)FC$=NF (8) (leading to 7); (2) F_4S=NF is more reactive than is F_2C=NF, thus favoring formation of SF_5NF^- over CF_3NF^-. Other reactions that were possible, but not observed, were fluoride-promoted destruction of F_4S=NF and displacements by CF_3NF^- on F_4S=NF.

Scheme I

In surprising contrast to the behavior noted for the reaction of F_4S=NF with F_2C=NF in the presence of active KF, it was found that the same reaction in the presence of active CsF led, not to compound 6, but to the unusual azo compound 9. We propose the mechanism outlined in Scheme I to explain the formation of 9. The initial step is essentially identical with that observed for the case where KF was used as the catalyst: displacement of F$^-$ from F_2C=NF by SF_5NF^-, forming 6. The more active CsF is able to further isomerize 6 to diaziridine 10. This postulate is supported by the fact that the analogous compound from the dimerization of F_2C=NF, 8, is readily isomerized by active CsF to the corresponding diaziridine, which in turn could be quantitatively isomerized to CF_3N=NCF$_3$ with Fe, Cr, or Ni metal. In the case described here, however, it appears that diaziridine 10 is unstable to further rearrangement, suffering ring opening followed by loss of F$^-$, yielding azo compound 9.

Strong support for the intermediacy of 6 in the formation of 9 was obtained in a separate experiment. Exposure of a sample of 6 to active CsF resulted in quantitative rearrangement of 6 to 9. An attempt at formation of the postulated intermediate 10, by use of the less active RbF, led only to slow formation of 9.

We believe compound 9 to be the first example of an azopentafluorosulfur species. It is a stable, volatile (extrapolated bp 16 °C), very pale yellow liquid that shows no tendency to degrade under the conditions of its synthesis. The ^{19}F NMR spectrum supports an all-trans structure for 9: a typical second-order pattern indicative of an SF$_5$ group is seen, with a slightly broadened (possibly due to the quadrupolar ^{14}N) singlet seen for the CF$_3$ group. If the configuration of 9 was cis, one might expect a more complex spectrum, due to through-space interaction of the SF$_5$ and CF$_3$ groups.

Addition of $XOSO_2F$ (X = Cl, Br, OSO_2F) to F_4S=NF. (Fluoroimido)tetrafluorosulfur reacted readily with $ClOSO_2F$ and $BrOSO_2F$ at low temperatures, and with FSO_2OOSO_2F at higher temperature, to form the unusual octahedral sulfur compounds cis-$SF_4(OSO_2F)NFX$. (One other addition of this type, that of ClF to $(CF_3)_3S$=NCF$_3$, to give the cis adduct, has been reported by other workers.[6a]) In the cases where $ClOSO_2F$ or $BrOSO_2F$ were used, transient color changes were noted when the reactants were mixed, indicating the possible intermediacy of polar species such as 11 or 12. The inter-

$$XOSO_2F^+\cdot SF_4NF^- \qquad\qquad F_4S=NXF^+FSO_3^-$$
$$\mathbf{11} \qquad\qquad\qquad \mathbf{12}$$

$$X = Br, Cl$$

mediate formed in the $ClOSO_2F$ case was very short-lived, being detected only by a brief flash of red color as the reactants mixed at low temperature. In contrast, the dark brown-violet species derived from the initial interaction of $BrOSO_2F$ and

Scheme II

Figure 1. Generalized structure of one enantiomer of the addition products derived from $F_4S{=}NF$ (X = Cl, Br, OSO_2F).
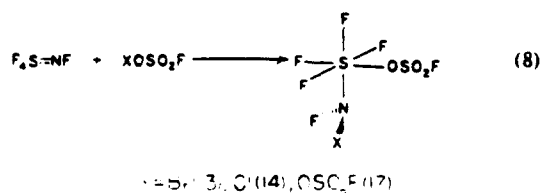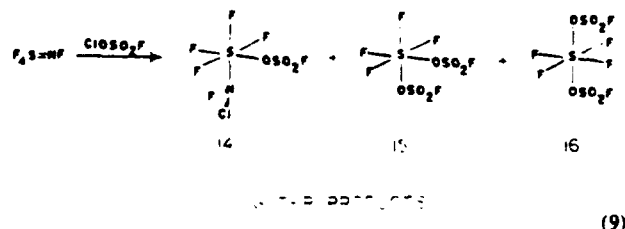
$F_4S{=}NF$ appeared to be stable indefinitely at -45 °C. Further warming caused the color to fade, with concomitant formation of colorless cis-$SF_4(OSO_2F)NBrF$ (**13**).

While cis-$SF_4(OSO_2F)NBrF$ was the only major heavy product formed in the reaction of $BrOSO_2F$ with $F_4S{=}NF$ (eq 8), an analogous situation was not seen for the reaction

of $ClOSO_2F$ with $F_4S{=}NF$. In this case, cis-$SF_4(OSO_2F)$-$NClF$ (**14**), cis-$SF_4(OSO_2F)_2$ (**15**), and $trans$-$SF_4(OSO_2F)_2$ (**16**) were obtained, in a molar ratio of 64:15:21 (eq 9). This

is apparently the first observation of $trans$-$SF_4(OSO_2F)_2$ (identified by NMR), though the cis isomer has long been known. The reason for the formation of these products in this case may lie in the apparent greater exothermicity of the reaction, compared to that of the $BrOSO_2F$ and FSO_2OOSO_2F reactions. Local heating could cause breakage of the S–N and/or N–Cl bonds of cis-$SF_4(OSO_2F)NFCl$, leading eventually to the observed products.

Compound **14** and especially compound **13** were thermally unstable at room temperature, decomposing with release of Cl_2 and Br_2, respectively. Thus, characterizations of **13** and **14**, as well as of cis- and $trans$-$SF_4(OSO_2F)_2$ (both admixed with **14**), were done by ^{19}F NMR, as described later.

Peroxydisulfuryl difluoride reacted (eq 8) smoothly with $F_4S{=}NF$, upon gradual warming, to afford cis-SF_4-$(OSO_2F)N(F)OSO_2F$ (**17**) in 71% yield. Unlike its halogenated analogues, **17** is thermally stable at 23 °C. It is a colorless liquid having an equilibrium vapor pressure of ca. 6 torr at 23 °C. It was characterized primarily by its infrared and ^{19}F NMR spectra. Neither chemical ionization nor electron impact mass spectra showed a molecular ion. This
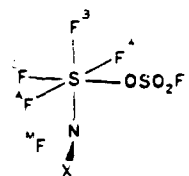
result is not surprising, as we have found this to be a general characteristic of covalent fluorosulfates.

The reaction of $F_4S{=}NF$ with the nonpolar but intensely reactive FSO_2OOSO_2F could proceed by a concerted addition of the peroxide to the double bond of $F_4S{=}NF$, by way of a radical ion or by a stepwise radical addition, as illustrated in Scheme II. The concerted process seems most likely, since the reaction is slower than the analogous reactions involving $BrOSO_2F$ and $ClOSO_2F$ (both polar molecular), and one would expect production of a mixture of cis- and $trans$-SF_4-$(OSO_2F)N(F)OSO_2F$ if the product were formed by way of cation **19** or radical **20**.

^{19}F NMR Spectra of cis-$SF_4(OSO_2F)NFX$ (X = Cl, Br, OSO_2F). The compounds **13**, **14**, and **17** have complex and highly characteristic ^{19}F NMR spectra, which establish the configurations of **13**, **14**, and **17** to be exclusively cis. In addition, the chemical shifts of fluorines A and A' (Figure 1) were found, for all three compounds, to be different. This difference is attributable to the influence of the neighboring chiral NFX group. Since N-fluoroamines are known to have high barriers to inversion, one would expect the NFX group to maintain its configuration, under the conditions of the measurements, thus providing a different magnetic environment for each of the fluorines A and A'.

The spectrum of **14** proved to be the most amenable to interpretation, even though it contained, in addition to the absorptions of **14**, those due to cis- (**15**) and $trans$-SF_4-$(OSO_2F)_2$ (**16**). Inspection of expanded segments of this spectrum (Figure 2) clearly shows the presence of the three major components (**14**, **15**, and **16**). The absorptions due to $trans$-$SF_4(OSO_2F)_2$ are straightforward: a simple triplet (Figure 2a) due to the SF_4 group and a simple quintet (Figure 2d) due to the two OSO_2F groups, with $^4J_{FF} = 7$ Hz. The spectrum of cis-$SF_4(OSO_2F)_2$ (Figure 2a,b,d) is more complex but is very similar to the 60-MHz spectrum of that compound reported in ref 11n.

Assignments of the resonances of cis-$SF_4(OSO_2F)NFCl$ were, despite the complexity of their fine structure, fairly straightforward. The integrated intensities allowed assignment of the central complex multiplets (Figure 2c) to fluorines A and A', although an actual distinction between the two cannot be made. The fluorosulfate multiplets occurred at values characteristic of that group (Figure 2d). The N–F absorption was distinguished by its broadness (due to quadrupolar effects of ^{14}N). The absorptions due to fluorines B and C were differentiated on the basis of two considerations. First, one would expect the fluorine B, cis to a fluorosulfate and three fluorines octahedrally coordinated to sulfur, to have a chemical shift in the same region as that of the similarly situated fluorines in cis-$SF_4(OSO_2F)_2$. This allows tentative assignment of the furthest downfield "quartet" to fluorine B. In addition, it was found that the chemical shifts of certain of the fluorines in this compound were markedly temperature dependent (this effect was even more pronounced for **13** and **17**). The furthest upfield "quartet" is shifted downfield, and the multiplets due to fluorines A and A' are shifted upfield, when the temperature is lowered. The far-downfield "quartet" is, in each case, only slightly affected. We assume that these effects are linked in some way to rotation of the NFCl group. If this is the case,
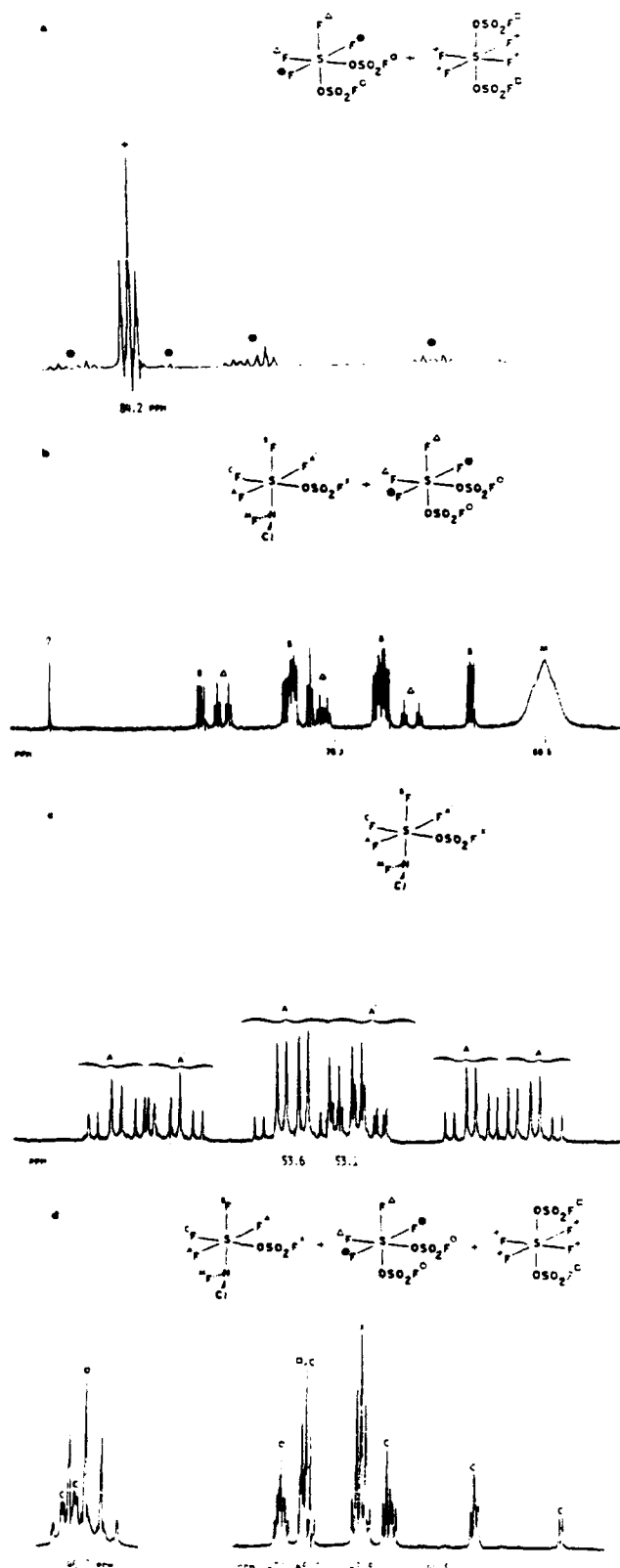
Figure 3. ^{19}F NMR (94.1 MHz) spectrum of cis-SF$_4$(OSO$_2$F)NBrF at -51 °C and 5000-Hz sweep width.

Figure 4. ^{19}F NMR (94.1 MHz) spectrum of cis-SF$_4$(OSO$_2$F)NF-(OSO$_2$F) at 30 °C and 2500-Hz sweep width.

one would expect the fluorines cis to the NFCl group to be the ones most affected, while the trans fluorine should be the least affected. This consideration allows assignment of the upfield "quartet" to fluorine C and also supports the earlier assignment of the downfield "quartet" to fluorine B.

The spectra of **13** and **17** were interpreted in an analogous manner. The spectra and details of the interpretations are shown in Figures 3 and 4.

Attempts at computer simulation of the NMR spectrum of **14** were only partly successful, with good agreement between all parts of the experimental and simulated spectra not being obtained. The appearance of the simulated spectra did support, however, the assignment of a 7.5-Hz coupling between the trans fluorines A and A' in compound **14**. Attempts at simulation of the spectra of **13** and **17** were not made, due to the difficulty of assigning the often badly overlapped lines.

Self-Reaction of F$_4$S=NF under F$^-$-Catalytic and Photolytic Conditions. One might suppose that F$_4$S=NF could be induced to form a linear dimer, SF$_5$NF(F$_3$)S=NF, by analogy with the previously mentioned fluoride–induced dimerization of F$_2$C=NF (eq 6 and 7). This expectation, however, was not realized. Instead, F$_4$S=NF, when allowed to interact with active KF, was destroyed fairly rapidly, with concomitant formation of N$_2$, SF$_4$, and SF$_6$. In some runs, small quantities of a heavier material were obtained. Analysis of this substance showed it to be not the expected dimer but, rather, the unusual amine (SF$_5$)$_2$NF (**21**), one of the few known examples[5] of the small class of geminal bis(pentafluorosulfur) compounds, some others being (SF$_5$)$_2$CF$_2$,[11m,21] (SF$_5$)$_2$NSCF$_3$,[5] (SF$_5$)$_2$NCl,[5] (SF$_5$)$_2$N$^-$,[5] and (SF$_5$)$_2$O.[22] The structure of (SF$_5$)$_2$NF was confirmed by comparison of its spectral properties with those

Figure 2. ^{19}F NMR (94.1 MHz) spectrum of a mixture of cis-SF$_4$(OSO$_2$F)$_2$, $trans$-SF$_4$(OSO$_2$F)$_2$, and cis-SF$_4$(OSO$_2$F)NFCl: (a) cis-SF$_4$(OSO$_2$F)$_2$ and $trans$-SF$_4$(OSO$_2$F)$_2$ (+) at -21 °C and 500-Hz sweep width; (b) cis-SF$_4$(OSO$_2$F)$_2$, F^B of cis-SF$_4$(OSO$_2$F)NClF (B), and F^M of cis-SF$_4$(OSO$_2$F)NClF (M) at -70 °C and 1000-Hz sweep width; (c) F^A and F$^{A'}$ of cis-SF$_4$(OSO$_2$F)NClF (A, A') at -70 °C and 500-Hz sweep width; (d) cis-SF$_4$(OSO$_2$F)$_2$, $trans$-SF$_4$(OSO$_2$F)$_2$, F^C of cis-SF$_4$(OSO$_2$F)NClF (C), and F^X of cis-SF$_4$(OSO$_2$F)NClF (X) at -70 °C and 1000-Hz sweep width (right), with a 250-Hz sweep width expansion of multiplet at δ 46.7 (left).

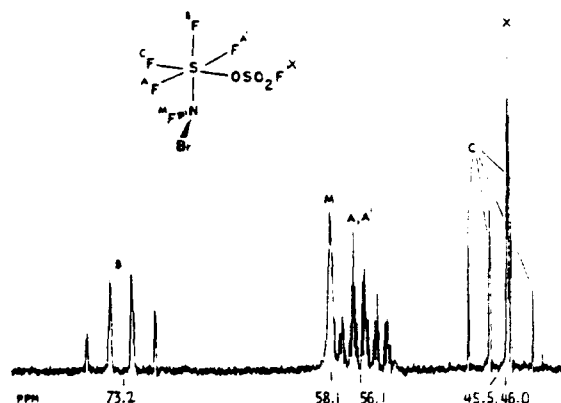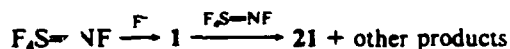(21) Shimp, L. A.; Lagow, R. J. *Inorg. Chem.* **1977**, *16*, 2974.
(22) (a) Roberts, H. L. *J. Chem. Soc.* **1960**, 2774. (b) Oberhammer, H.; Seppelt, K. *Inorg. Chem.* **1978**, *17*, 1435.

recently reported for it by others,[5] who obtained it by the reaction of $Cs^+(SF_5)_2N^-$ with F_2.

The mechanism for the formation of **21** is clearly complex and may well be due to the formation of an intermediate anion, $SF_5NFSF_4NF^-$, in analogy to the formation of $CF_3NFCF_2NF^-$ from $F_2C=NF$ and F^-:

$$F_4S=NF \xrightarrow{\ F^-\ } 1 \xrightarrow{\ F_4S=NF\ } 21 + \text{other products}$$

In contrast to its chlorinated analogue, $F_4S=NCl$,[23] which spontaneously dimerizes to a cyclic four-membered ring compound, $(F_4SNCl)_2$,[11q] $F_4S=NF$ shows no tendency to form such a dimer, even when heated. In another attempt to induce

dimerization, photolysis of $F_4S=NF$ was tried. After 1 h of ultraviolet irradiation through Pyrex glass, $F_4S=NF$ was recovered unchanged. Irradiation through quartz resulted in partial decomposition of $F_4S=NF$, with production of products similar to those found after its decomposition in the presence of KF. These included SF_4, SF_6, N_2, and, interestingly, $(SF_5)_2NF$ **(21)**. In this case, the formation of **21** may proceed by a mechanism similar in many respects to that proposed by others[5a,c,d,f] for the formation of $F_4S=NSF_5$ from F_2 and NSF_3.

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(23) $SF_4=NCl$ has never been isolated, but it is assumed to be the precursor to the cyclic dimer.[11q]

NOVEL AMMONIUM HEXAFLUOROARSENATE SALTS FROM REACTION OF $(CF_3)_2NH$, $CF_3N(OCF_3)H$, $CF_3N[OCF(CF_3)_2]H$, CF_3NHF AND SF_5NHF WITH THE STRONG ACID HF/AsF_5.

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SUMMARY

Reactions of the fluorinated amines $(CF_3)_2NH$, $CF_3N(OCF_3)H$, $CF_3N[OCF(CF_3)_2]H$, CF_3NHF and SF_5NHF with the strong acid HF/AsF_5 form the corresponding ammonium salts $R_f^1R_f^2NH_2^+AsF_6^-$ and $R_fNFH_2^+$-AsF_6^- in high yield. [$R_f^1=CF_3$, $R_f^2=CF_3$, CF_3O, $(CF_3)_2CFO$; $R_f=CF_3$, SF_5] The colorless crystalline solids are stable for prolonged periods at 22°C in sealed FEP containers. They have dissociation pressures at 22°C ranging from ~5 torr ($R_fNFH_2^+AsF_6^-$) to ~50 torr [$CF_3N(OCF_3)H_2^+AsF_6^-$]. ^{19}F NMR and Raman spectroscopy were used to identify the compounds.

INTRODUCTION

Fluoroammonium salts of the type NFH_3^+, $NH_2F_2^+$ and NF_4^+ are well known and $NH_2F_2^+$ can be prepared directly from NF_2H by protonation in superacid media HF/MF_5 (M=As, Sb) [2,3]. On the other hand, NF_3 cannot be converted to NF_3H^+ in the same way. Similarly, it is well known that fluorocarbon amines such as $(CF_3)_3N$ and $(CF_3)_2NH$ have very low basicity, but there do not appear to have been any attempts to protonate these and related compounds in superacid media.

During investigations of the chemistry of CF_2=NF [4], we attempted to form a cation of the imine by removal of a fluoride ion with AsF_5. Instead of the desired salt, CF_2=NF and AsF_5 formed a weak molecular complex at lower temperature which was completely dissociated at 22°C. While attempting to characterize this complex by NMR, we inadvertently prepared $CF_3NFH_2^+$ in fluorosulfuric acid solution. This result prompted us to investigate the obvious question as to whether fluorocarbon amines would form stable ammonium salts. Using several fluorocarbon amines available from on-going research, we report here the facile formation of ammonium hexafluoroarsenate salts by reaction of $(CF_3)_2NH$, $CF_3N(OCF_3)H$, $CF_3N[OCF(CF_3)_2]$, CF_3NFH and SF_5NHF with the strong acid HF/AsF_5.

EXPERIMENTAL

General

All volatile compounds were handled in glass or stainless steel vacuum systems equipped with glass-Teflon and severe service stainless steel valves, respectively. Amounts of materials were measured by PVT measurements or direct weighing. Pressures were measured with a Wallace and Tiernan differential pressure gauge, series 1500. Temperatures were measured with a digital-indicating iron-constantan thermocouple.

Infrared spectra were taken on a Perkin-Elmer 1430 instrument with a 3600 Data Station. Spectra involving HF were taken with 5 cm stainless steel or 10 cm Teflon-Kel-F cells fitted with AgCl windows. Other spectra were taken in 10 cm glass cells fitted with KCl or AgCl windows. ^{19}F NMR spectra were taken on Varian XL-100-15, JEOL C-60-HL or JEOL FX-90Q spectrometers with external $CFCl_3$ as a reference. Chemical shifts are in ppm relative to external $CFCl_3$, with high field shifts having a negative sign. Solutions

involving HF were contained in 4 mm OD thin wall Kel-F tubes inserted

in a standard 5 mm glass NMR tube. The Kel-F tubes were filled

by vacuum transfer and sealed before inserting them into the glass

NMR tube. Raman spectra were taken using thin wall FEP tubes for

sample containers, utilizing a Spex 14018 double monochromator with

photon-counting detection. Excitation was via the 514.5-nm line

of an Ar^+ ion laser.

Reagents

The amines $(CF_3)_2NH$ [5], $CF_3N(OCF_3)H$, $CF_3N[OCF(CF_3)_2]H$,

CF_3NHF [6] and SF_5NHF [7], and the imines $CF_2=NF$ [4] and $SF_4=NF$ [7] were

prepared by literature methods. Hydrogen fluoride was obtained from Air

Products Inc. and was purified by distillation. Arsenic pentafluoride

was prepared by heating reagent grade As_2O_5 with excess fluorine

at 200° in a Monel bomb.

Synthesis of ammonium salts

In a typical reaction, 1 ml of HF was distilled into a 10 ml FEP reactor

at -196°C, followed by 3.0 mmol of AsF_5. The mixture was warmed to 22°C to form

a solution of AsF_5 in HF. The reactor was then cooled to -196° and perfluoro-

methanimine (3.0 mmol) was added. The mixture was warmed to 22°C

and let stand for 1 h. It was then cooled to -70°C and pumped on

through an FEP U-trap. Pumping to constant weight at this temperature

resulted in a fine white crystalline solid corresponding to 94%

yield of $CF_3NFH_2^+AsF_6^-$ based on the starting $CF_2=NF$. Similar results

were obtained starting with CF_3NHF. Other salts were prepared from

the amines using similar procedures. When pumped on at -78°C to

remove excess HF, the yields were quantitative within experimental

error. All the salts sublimed readily at 22°C in sealed FEP containers

to form large transparent crystals.

$CF_3{}^A NF^B H_2{}^+ AsF_6{}^-$: $P_{22°C} \simeq 7$ torr; NMR (HF, -34°C) A -74.5(d), B -92.2(q); $J_{AB} = 17.5$ Hz; Raman(s) 1291(w), 1200(w), 961(w), 773(vw), 667(s), 639(w), 493(w), 451(s), 442(sh), 394(m), 340(w), 288(vw) cm^{-1}.
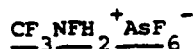
$F^A SF_4{}^B NF^X H_2{}^+ AsF_6{}^-$: $P_{22°C} \simeq 7$ torr; NMR (HF, -52°C) A 52(m), B 51.7(m), X -68.9(br, s); $J_{AB} \simeq 150$, J_{BX} and J_{AX} not readily determined; Raman(s) 1064(m), 753(s), 692(s), 666(m), 564(w), 521(w), 449(m), 379(w), 371(m), 119(w), 79(w) cm^{-1}.

$CF_3 N(OCF_3)_3 H_2{}^+ AsF_6{}^-$: $P_{22°C} \simeq 50$ torr; NMR not determined; Raman (s, -196°C) 1245(vw), 1185(vw), 1162(vw), 1054(w), 909(s), 773(w), 709(s), 690(sh), 685(s), 574(m), 333(w), 297(w), 221(w), 192(vw) cm^{-1}.
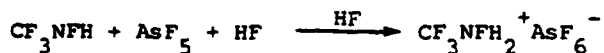
$(CF_3{}^A)_2 NH_2{}^+ AsF_6{}^-$: $P_{22°C} \simeq 20$ torr; NMR (HF, -28°C) A -58.3(s); Raman not determined.

$CF_3 N[OCF(CF_3)_3]_2 H_2{}^+ AsF_6{}^-$: $P_{22°C} \simeq 10$ torr; other data not determined.

RESULTS AND DISCUSSION

$CF_3 NFH_2{}^+ AsF_6{}^-$

The formation of fluorotrifluoromethylammonium hexafluoroarsenate, $CF_3 NFH_2{}^+ AsF_6{}^-$, occurs in high yield on reaction of either $CF_2 = NF$ or $CF_3 NFH$ with a stoichiometric amount of AsF_5 in excess liquid HF at or below 22°C. Excess AsF_5 can also be employed with similar results.

$$CF_2 = NF + HF \longrightarrow CF_3 NFH$$

$$CF_3 NFH + AsF_5 + HF \xrightarrow{HF} CF_3 NFH_2{}^+ AsF_6{}^-$$

Removal of the excess HF at -70°C gives a nearly quantitative yield of the ammonium salt. The HF can also be removed near 0°C with a resulting lower yield of the salt. At this temperature, the salt

already has a measurable dissociation pressure and some of the starting

amine and AsF_5 are removed along with HF. At 22°C, the dissociation

pressure is ≈7 torr and the IR spectrum of the equilibrium vapor is

that of CF_3NFH and AsF_5. At this pressure the HF is not visible, but

its presence is readily discernible by its attack on glass forming

SiF_4.

Support for the structure of $CF_3NFH_2^+AsF_6^-$ comes from the

Raman and ^{19}F nmr spectra. Raman spectra were only of marginal

quality because of strong fluoresence in all samples under a variety

of conditions, including low temperature Kel-F, FEP or Pyrex sample

containers, HF solutions and varying the wavelength of the laser

excitation. Nevertheless, sufficient quality spectra could be obtained

to readily assign ν_1 of AsF_6^- at 667 cm^{-1} as the most intense band

in the spectrum of the solid. This value compares favorably with

related AsF_6^- salts of $NF_2H_2^+$ and NF_4^+ [8]. * Other observed bands

are reasonable for the salt but no effort was made to assign them.

The strongest support for the cation $CF_3NFH_2^+$ comes from its

^{19}F NMR. In HF solution, $CF_3NFH_2^+AsF_6^-$ shows a doublet for the

CF_3 (-74.5) and a quartet for the fluorine on nitrogen (-92.2) with

$^3J_{FF}$ = 17.5 Hz. Cooling to as low as -70°C did not result in any

observable J_{HF} coupling. This is in contrast to the free amine

in $CFCl_3$, where a doublet of doublets is observed for the CF_3 (-74.2)

and a doublet of quartets for the NF (-126.7), with $^3J_{FF}$ = 26.7,

$^2J_{H-NF}$ = 9.5 and $^3J_{H-CF_3}$ = 9.5 Hz [6]. Clearly, $CF_3NH_2F^+$ is exchanging

protons with the solvent HF and the concentrations of both $CF_3NFH_2^+$

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* The ν_1 band for $NF_2H_2^+AsF_6^-$ occurs at 714 and 674 cm^{-1}
and a frequency of 667 cm^{-1} for $CF_3NFH_2^+AsF_6^-$ is very reasonable.
See ref. 2 and references therein.

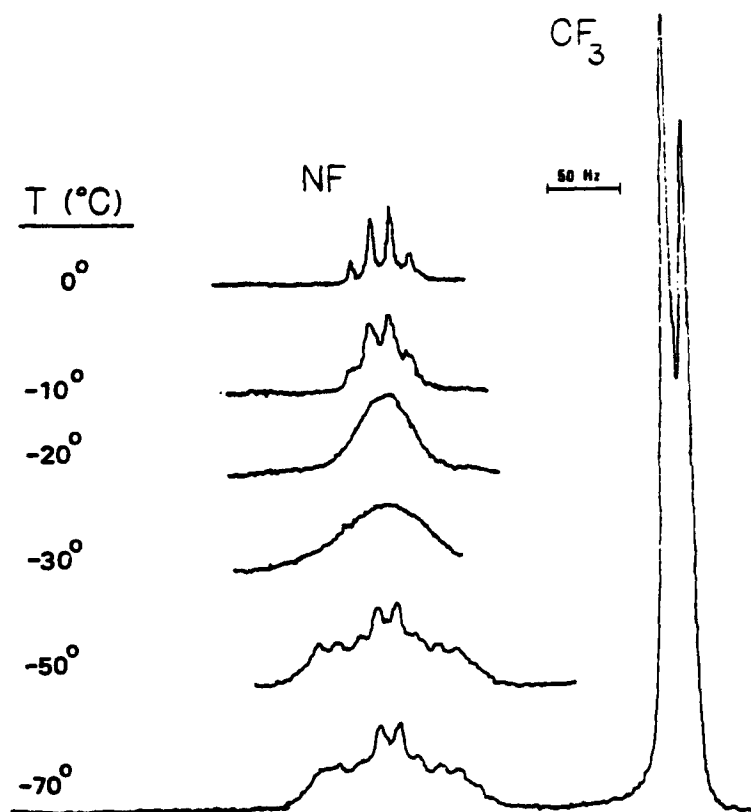Fig. 1. ^{19}F NMR OF $CF_3NFH_2^+AsF_6^-$ in $HOSO_2F$. 1000 Hz sweep
width. Relative area $NF:CF_3$=1.0:3.0. CF_3 signal shows little
change with temperature.

and CF_3NHF may be comparable*. The latter conclusion is supported
by the ^{19}F NMR of $CF_3NFH_2^+AsF_6^-$ in fluorosulfuric acid. The temperature
dependent spectrum is shown in Figure 1. The doublet of relative
area 3 due to the CF_3 (-69) and the triplet of quartets of relative
area 1, due to the NF (-65) can be explained by $^3J_{FF}$ = 14 and $^2J_{H-NF}$ ≃42
Hz**. The large change in the chemical shift of the NF group, and
the observable $^2J_{HF}$ coupling, clearly imply that the species is

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* Proton exchange of $NH_2F_2^+AsF_6^-$ in HF could be suppressed by
  addition of excess AsF_5 to the solution (ref. 2). We attempted
  this with $CF_3NFH_2^+AsF_6^-$ without success.

** In a sample of $CF_3NFH_2^+AsF_6^-$ in $HOSO_2F$ at 30°C, the AsF_6^-
  anion is visible as a very broad signal near -63 ppm.

predominantly the $CF_3NFH_2^+$ cation in $HOSO_2F$ and its exchange of protons with the solvent is slow on the NMR time scale at lower temperatures. This is in contrast to HF as a solvent where the exchange is fast and where CF_3NHF is probably a major species. If the latter is true, the chemical shift of the NF group in HF might be expected somewhere between that of pure CF_3NHF (-126.7) in $CFCl_3$ and $CF_3NFH_2^+$ (-65) in $HOSO_2F$. Fortuitously, it is found at -92, very near the average of the two values.

Other examples of fluorinated ammonium salts

Other ammonium salts can be similarly formed from $(CF_3)_2NH$, $CF_3N(OCF_3)H$, $CF_3N[OCF(CF_3)_2]H$ and $SF_4=NF$ or SF_5NHF. The least stable salt was observed with $CF_3N(OCF_3)H$, which exhibited the highest dissociation pressure at 22°C. The stability of $SF_5NFH_2^+AsF_6^-$ was similar to that of $CF_3NFH_2^+AsF_6^-$. The Raman spectra for $CF_3N(OCF_3)H_2^+$-AsF_6^- and $SF_5NFH_2^+AsF_6^-$ both contained strong bands assignable to ν_1 of AsF_6^- at 690 and/or 685, and 692 and/or 666 cm^{-1}, respectively. The ^{19}F NMR spectra of $(CF_3)_2NH_2^+AsF_6^-$ and $SF_5NFH_2^+AsF_6^-$ in HF solution are similar to that of $CF_3NFH_2^+AsF_6^-$ in HF. The $^3J_{HF}$ coupling readily observed in $(CF_3)_2NH$ is absent in the solution of the ammonium salt and the chemical shift of CF_3 groups is only slightly different from that of the free amine (-58.3 vs. -57.1). Similarly, $^2J_{HF}$ is not observable for $SF_5NFH_2^+AsF_6^-$. As with CF_3NFH, a substantial change is observed for the NF chemical shift in $SF_5NFH_2^+$ (-68.9) vs. pure SF_5NHF (-74.7). The shift in the axial S-F fluorines of SF_5 group is even larger (52 vs. 64.6), whereas the equitoral fluorines show little change (51.7 vs. 52.6).

CONCLUSION

The facile formation of fluorinated alkyammonium hexafluoro-arsenate salts has been demonstrated by reaction of fluorinated amines with AsF_5/HF. While only a few examples have been prepared it seems clear that a variety of amines of the type R_fNFH and $R_f^1R_f^2NF$ will react similarly. It would be of interest in the future to determine if related compounds such as R_fNF_2, $(R_f)_2NF$ and $(R_f)_3N$ will also form ammonium salts under similar conditions.

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8   K. O. Christe and D. Pilipovich, Inorg. Chem., 10 (1971) 2803. ν_1 of AsF_6^- in $NF_4^+AsF_6^- = 685$ cm^{-1}.

An Efficient Synthesis of N-Bromoperhalo-1-alkanimines

Summary: Certain perhalogenated nitriles have been found to react readily with bromine and active cesium fluoride to afford high yields of N-bromoperhalo-1-alkanimines ($R_xFC=NBr$; $R_x = CF_3$, C_2F_5, n-C_3F_7, CF_2Cl, CCl_3). Photolysis of the perfluorinated N-bromo compounds affords the novel perfluoroazines $R_fFC=NN=CFR_f$.

Sir: A number of N-bromoperhalo-1-alkanimines ($R_xFC=NBr$) have long been known, but their chemistry has remained unexplored due to the inefficiency of the reported syntheses.[1] Here we report a simple, high-yield synthesis of five of these compounds by reaction of the corresponding perhalogenated nitriles with bromine and active cesium fluoride. These reactions probably proceed by initial formation of $R_xFC=N^-$, followed by oxidation of the intermediate anion by bromine to afford $R_xFC=NBr$. This postulate is supported by mechanistically similar chemistry reported for other unsaturated perfluorinated systems.[2]

The preparation of $CF_3FC=NBr$ (1) is described as a typical example. (*CAUTION!* Many N-halo compounds are known to be powerful explosives. We have experienced no explosions during the preparation and handling of the N-bromoperhalo-1-alkanimines, but the potential instability of these compounds and certain of their derivatives should be kept in mind. We advise that preparations and reactions of these materials be done on a small scale.) Trifluoroacetonitrile (15 mmol) and then bromine (30 mmol)[3] were condensed into a 100-mL Pyrex flask containing active cesium fluoride (35 mmol)[4] and fitted with

(1) (a) Tullock, C. W. Brit. Pat. 870 328, 1968. See also: *Chem. Abstr.* **1962**, *56*, 8561*f*. (b) Chambers, W. J.; Coffman, D. D. U.S. Pat. 3 023 208, 1962. See also: *Chem. Abstr.* **1962**, *57*, 11215. (c) Tullock, C. W. U.S. Pat. 3 057 849, 1962. See also: *Chem. Abstr.* **1963**, *58*, 3315*b*. (d) Chambers, W. J.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* **1962**, *84*, 2337.

(2) Chambers, R. D. "Fluorine in Organic Chemistry"; Wiley: New York, 1973.

(3) The excess bromine is eventually absorbed by the solid phase. Presumably, CsBr₃ and higher cesium polybromides are formed.

(4) The cesium fluoride was activated by fusion in a platinum dish, followed by grinding to a fine powder in a ball mill under dry nitrogen.

Table I. Spectral Data for N-Bromoperhalo-1-alkanimines

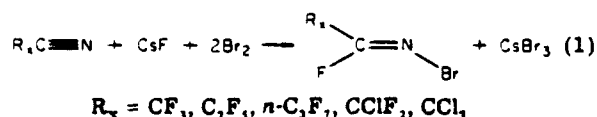| compound	^{19}F NMR;[a] solvent	IR ($\nu_{C=N}$, cm^{-1})
1, CF$_3$^{A}F^{M}C=NBr	F^A −71.8; F^M −27.5; J_{AM} 5.5 Hz; CFCl$_3$[b]	1705[b]
2, CF$_3$^{B}CF$_2$^{A}F^{M}C=NBr	F^A −118.7; F^B −83.55; F^M −21.76; J_{AB} 2, J_{AM} 16, J_{BM} 5 Hz; CDCl$_3$	1695
3, CF$_3$^{C}CF$_2$^{B}CF$_2$^{A}F^{M}C=NBr	F^A −116.2; F^B − 127.3; F^C −81.23; F^M −19.95; J_{AM} 13, J_{BM} 6.5, J_{AC} 8, others ≤ 2 Hz; CCl$_4$/CDCl$_3$ (9:1)	1690
4, CClF$_2$^{A}F^{M}C=NBr	^{A}F −60.02; ^{M}F −26.70; J_{AM} 11 Hz; CDCl$_3$	1695
5, CCl$_3$F^{M}C=NBr	F^M −24.32; acetone-d_6	1670

[a] 90-MHz NMR in ppm; CFCl$_3$ internal reference. [b] Chang, S.-C.; DesMarteau, D. D. *Inorg. Chem.* 1983, 22, 805.

Table II. Spectral Data for Perfluoroazines

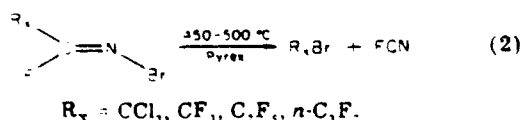| compound	^{19}F NMR;[a] solvent	IR ($\nu_{C=N}$, cm^{-1})
6, (CF$_3$^{A}F^{M}C=N)$_2$	F^A −72.70; F^M −62.22; J_{AM} 11 Hz; CCl$_4$ CCl$_4$/CDCl$_3$ (9:1)	1720
7, (CF$_3$^{B}CF$_2$^{A}F^{M}C=N)$_2$	F^A −120.2; F^b − 83.14; F^M −55.94; J_{AB} 2, J_{AM} 14.5, J_{BM} 4.5 Hz; CDCl$_3$	1710
8, (CF$_3$^{C}CF$_2$^{B}CF$_2$^{A}F^{M}C=N)$_2$	F^A −118.4; F^B −127.3; F^C − 81.01; F^M − 55.46; J_{AC} 9, J_{AM} 13, J_{BM} 10, others ≤ 2 Hz; CDCl$_3$	1710

[a] 90-MHz NMR in ppm; CFCl$_3$ internal reference.

a glass-Teflon stopcock. As the bromine melted, the flask was rotated so as to distribute the Br$_2$/CsF in a thin layer. The reaction became mildly exothermic, and most of the free bromine appeared to have been consumed within 5 min. The mixture was left in darkness for 16 h at 23 °C. Trap-to-trap fractionation (−93, −196 °C) gave CF$_3$FC=NBr, slightly contaminated with bromine, in the −93 °C trap. Unreacted CF$_3$CN collected in the −196 °C trap. The bromine was removed by brief exposure of the mixture to an excess (~8 mmol) of ethylene, followed by trap-to-trap fractionation: −54 °C (C$_2$H$_4$Br$_2$), −90 °C (CF$_3$FC=NBr; 11.8 mmol, 79% yield), −196 °C (C$_2$H$_4$). The compounds C$_2$F$_5$FC=NBr (2), n-C$_3$F$_7$FC=NBr (3), CClF$_2$FC=NBr (4), and CCl$_3$FC=NBr (5) were obtained in a similar fashion (eq 1).

$$R_xC≡N + CsF + 2Br_2 \longrightarrow \underset{F}{\overset{R_x}{>}}C≡N_{Br} + CsBr_3 \quad (1)$$

R$_x$ = CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$, CClF$_2$, CCl$_3$

We attempted to prepare CH$_3$FC=NBr and C$_6$F$_5$FC=NBr from CH$_3$CN and C$_6$F$_5$CN, respectively, without success. These results indicate that a highly halogenated aliphatic group, R$_x$, is necessary for preparation of R$_x$FC=NBr under our conditions.

The N-bromoperhalo-1-alkanimines were readily characterized by their ^{19}F NMR and IR spectra (Table I). The fluoroalkyl NMR absorptions all appear as simple first-order patterns. The "vinylic" fluorines (F^M) characteristically give rise to broad peaks near δ −20 (R$_x$F^{M}C=NBr). The NMR spectra indicate that imines 1-5 exist in only one of two possible isomeric forms. We assume, on steric grounds, that the observed isomer is, in each case, the one with the bromine atom anti to the perhaloalkyl group. Compounds 1-5 are thermally stable (CF$_3$FC=NBr survives prolonged heating at 200 °C). Pyrolysis at higher temperatures (450–500 °C, Pyrex flow system) affords a mixture of perhaloalkyl bromide and cyanogen fluoride (eq 2).

$$\underset{F}{\overset{R_x}{>}}C≡N_{Br} \xrightarrow[\text{Pyrex}]{450-500 \text{ °C}} R_xBr + FCN \quad (2)$$

R$_x$ = CCl$_3$, CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$.

The N-bromo imines are moderately light-sensitive. The light-sensitivity of compounds 1-3 was exploited in the preparation of the perfluorinated azines 6-8.[5] Ultraviolet photolysis (250-W medium-pressure mercury lamp) of the bromo imines affords a mixture consisting primarily of azine, bromine, and starting materials (eq 3). This be-

$$2\underset{F}{\overset{R_f}{>}}C=N_{Br} \xrightarrow[\text{Pyrex}]{h\nu} \underset{R_f}{\overset{F}{>}}C=N-N=C\underset{F}{\overset{R_f}{<}} + Br_2 \quad (3)$$

R$_f$ = CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$

havior parallels that seen for (CF$_3$)$_2$C=NBr, which, upon photolysis, affords (CF$_3$)$_2$C=NN=C(CF$_3$)$_2$ and Br$_2$.[6] In the cases described here, however, the photolytic conversion is not as efficient as that reported for the preparation of (CF$_3$)$_2$C=NN=C(CF$_3$)$_2$. In this work, as the concentrations of azine and bromine build up, significant competing reactions begin to occur.[7] These competitive processes can be partly overcome by periodic removal of the bromine, using either ethylene or propylene, but complete conversion of bromo imine to azine is never achieved. Removal of unreacted bromo imine is done by reaction with mercury (to yield the corresponding nitrile); the nitrile and azine are then separable by vacuum-line fractionation or by preparative GLC. The purified products are readily characterized by their ^{19}F NMR and IR spectra (Table II).

Further studies of the reactions of the N-bromoperhalo-1-alkanimines (such as those with olefins, to yield R$_x$FC=NCYY'CZZ'Br, and with CO, to yield 1-bromoperhaloalkyl isocyanates), and of the products derived from them, are in progress.

(5) Some of these azines have been prepared by reaction of appropriate perfluorinated diazenes with metal carbonyls: (a) Chambers, W. J. U.S. Pat. 3 117 996, 1964. See also: ref 1d and *Chem. Abstr.* 1964, 60, 6745e. (b) Compound 6 has recently been prepared from CF$_3$ClC=NN=CClCF$_3$ and KF: Barlow, M. J.; Bell, D.; O'Reilly, N. J.; Tipping, A. E. *J. Fluorine Chem.* 1983, 23, 293.

(6) Middleton, W. J.; Krespan, C. G. *J. Org. Chem.* 1965, 30, 1398.

(7) The competing reactions yield colorless, crystalline solids of slight volatility. The structures of these products are unclear at present, but we have determined that, in the case where R$_f$ = CF$_3$, the material contains both bromine (produced by slow decomposition of the material at 23 °C in room light) and the CF$_3$FC=N group (observed in the mass spectrum of the vapor).

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Received January 30, 1984

Synthesis of CF$_3$NBr$_2$ and CF$_3$NBrCl. Novel Metal Fluoride Promoted Conversion of N–Cl Bonds to N–Br Bonds
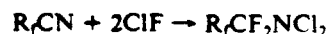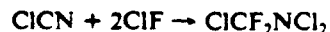
Sir:

The synthesis of fluorinated compounds containing the N,N-dichloro group is readily accomplished by the addition

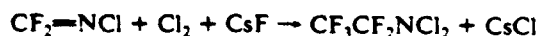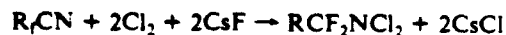**Table I.** Metal Fluoride Promoted Reactions of N–Cl with Br$_2$

N–C (amt^a)	Br$_2$/MF^a	t^b	products^a CF$_3$· NBrCl	CF$_3$· NBr$_2$
CF$_2$=NCl (2.0)	1.7/8.5 (CsF)	11	0.4	0.6^c
CF$_2$=NCl (2.0)	4.0/9.2 (CsF)	11	0.9	0.6^d
CF$_2$=NCl (2.0)	2.0/20 (CsF)	12	0.8	d
CF$_3$NClBr (0.6)	10/10 (CsF)	12		0.5^c
CF$_3$NClBr (0.5)	10/20 (CsF)	12		0.1^c
CF$_3$NCl$_2$ (1.0)	10/10 (CsF)	42	0.2	0.3^c
CF$_3$NCl$_2$ (1.0)	10/20 (CsF)	40	0.3	0.1^c
CF$_3$NCl$_2$ (0.9)	10/10 (KF)	40	0.4	trace^c
CF$_3$NCl$_2$ (1.0)	10/10 (NaF)	40	0.5	c
CF$_3$NCl$_2$ (1.0)	10/10 (LiF)	40	0.2	c
CF$_3$NCl$_2$ (1.0)	10/10 (CaF$_2$)	40		c

^{a} Amounts in millimoles. ^{b} Time in hours in the absence of light at 22 °C. ^{c} Starting NCl recovered. ^{d} Some CF$_3$NCl$_2$ formed.
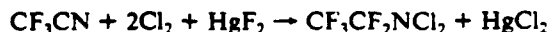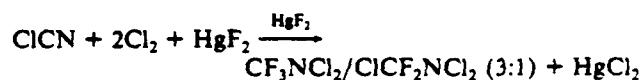
of ClF to a variety of carbon–nitrogen multiple bonds.[1] For example, the following reactions proceed in high yield:[2–4]

$$ClCN + 2ClF \rightarrow ClCF_2NCl_2$$

$$R_fCN + 2ClF \rightarrow R_fCF_2NCl_2$$

$$CF_2\!\!=\!\!NCl + ClF \rightarrow CF_3NCl_2$$

We have recently shown that the cesium fluoride promoted chlorination of C–N multiple bonds with Cl$_2$ is also an effective method for the synthesis of the same compounds.[5]

$$R_fCN + 2Cl_2 + 2CsF \rightarrow RCF_2NCl_2 + 2CsCl$$

$$CF_2\!\!=\!\!NCl + Cl_2 + CsF \rightarrow CF_3CF_2NCl_2 + CsCl$$

In related work, HgF$_2$ has also been shown to be effective in these transformations, where the HgF$_2$/Cl$_2$ mixture behaves as an in situ source of ClF.[6]

$$ClCN + 2Cl_2 + HgF_2 \xrightarrow{HgF_2}$$
$$CF_3NCl_2/ClCF_2NCl_2 \ (3:1) + HgCl_2$$

$$CF_3CN + 2Cl_2 + HgF_2 \rightarrow CF_3CF_2NCl_2 + HgCl_2$$

The latter reaction could also be extended to Br$_2$ to yield both CF$_3$CF$_2$NBr$_2$ and CF$_3$CF=NBr and represented the first example of a thermally stable NBr$_2$ derivative. Cesium fluoride is also effective in promoting the reaction of Br$_2$ with C–N multiple bonds, but in the case of nitriles the reaction stops at the imine.[5,7]

$$CF_2\!\!=\!\!NF + 2Br_2 + CsF \rightarrow CF_3NBrF + CsBr_3$$

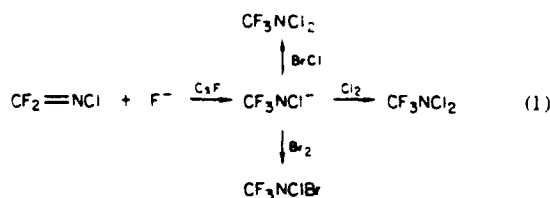$$CF_3CN + 2Br_2 + CsF \rightarrow CF_3CF\!\!=\!\!NBr + CsBr_3$$

We were interested in preparing the first example of a stable compound containing an –NClBr function, and we investigated the CsF-promoted reaction of Br$_2$ with CF$_2$=NCl.[8] The reaction worked well, but to our surprise, CF$_3$NBr$_2$ was also formed.

$$CF_2\!\!=\!\!NCl \xrightarrow{Br_2/CsF} CF_3NBrCl + CF_3NBr_2$$

(1) Schack, C. J.; Christe, K. O. *Isr. J. Chem.* **1978**, *17*, 20
(2) Young, D. E.; Anderson, L. R.; Fox, W. B. *J. Chem. Soc., Chem. Commun.* **1970**, 395.
(3) Hynes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.
(4) Swindell, R. F.; Zaborowski, L. M.; Shreeve, J. M. *Inorg. Chem.* **1971**, *10*, 1635.
(5) Chang, S.-C.; DesMarteau, D. D. *Inorg. Chem.* **1983**, *22*, 805.
(6) Waterfeld, A.; Mews, R. *J. Chem. Soc., Chem. Commun.* **1982**, 839.
(7) High-yield syntheses of a variety of R$_f$CF=NBr compounds are reported in: O'Brien, B. A.; DesMarteau, D. D., to be submitted for publication.
(8) As far as we could determine, there are no reported examples of the isolation of –NBrCl derivatives.

Caution! While we have experienced no explosions during the handling of small quantities of these materials, many structurally similar *N*-halo compounds are known to be powerful explosives. Due caution must be exercised while conducting experiments such as those described here. In a typical reaction, CF_2=NCl, Br_2, and CsF were allowed to react in a 100-mL glass reactor containing a Teflon-coated magnetic stirring bar at 22 °C in the absence of light. The mixture was stirred for an appropriate time, and the products were then separated by pumpng through a series of cold traps. Essentially pure CF_3NClBr and CF_3NBr_2 were then obtained by brief treatment with excess C_2H_4 at 22 °C to remove unreacted Br_2, followed by reseparation. The reactions are summarized in Table I.

The formation of CF_3NBrCl can be explained by oxidation of the intermediate anion CF_3NCl^- by Br_2, in the same way that CF_3NCl_2 is formed from Cl_2 and CF_2=NCl (eq 1) and CF_3NBrF from Br_2 and CF_2=NF (eq 2).[5] In the above examples, there is no reaction in the absence of CsF.

$$CF_2\!=\!NCl + F^- \xrightarrow{\ CsF\ } CF_3NCl^- \xrightarrow{\ Cl_2\ } CF_3NCl_2 \quad (1)$$

with the intermediate branching to CF_3NCl_2 (via BrCl) and CF_3NClBr (via Br_2)

$$CF_2\!=\!NF + F^- \xrightarrow{\ CsF\ } CF_3NF^- \xrightarrow{\ Br_2\ } CF_3NFBr \quad (2)$$

The formation of CF_3NBr_2 in the reaction of CF_3NCl^- with Br_2 requires a substitution of Cl by Br in CF_3NBrCl. We have found that this substitution can be readily accomplished in both CF_3NBrCl and CF_3NCl_2 by reaction with Br_2 in the presence of CsF.

$$CF_3NCl_2 \xrightarrow{\ CsF/Br_2\ } CF_3NBrCl \xrightarrow{\ CsF/Br_2\ } CF_3NBr_2$$

There is no reaction under the same conditions in the absence of CsF, and CsF alone is also unreactive. Similarly, BrCl does not form a significant amount of either CF_3NBrCl or CF_3NBr_2 in the presence of CsF, and it converts CF_3NBrCl back to CF_3NCl_2.[9] The active species in these reactions may be $CsF\cdot Br_2$, which may contain a significant concentration of the anion FBr_2^-.[10] Very active CsF readily absorbs bromine to form a bright yellow-orange solid with only a small equilibrium pressure of Br_2 at 22 °C.[11] The Br_2 is removed very slowly by pumping on the solid under dynamic vacuum at 22 °C, and even heating at 100 °C will not readily remove all the Br_2. Active KF also absorbs Br_2 but to a lesser degree.[11] Potassium fluoride with Br_2 is only effective in converting CF_3NCl_2 to CF_3NBrCl and not to CF_3NBr_2.

We expected that NaF and LiF would be ineffective in promoting the reaction of CF_3NCl_2 with Br_2. However, both result in reasonable yields of CF_3NClBr (see Table I). To ascertain whether the formation of CF_3NClBr was a surface reaction only and not due to the metal fluoride itself, we tried CaF_2 under the same conditions and it was unreactive. This result, combined with the fact that the formation of CF_3NBr_2 is only observed with CsF, would suggest that these reactions are fluoride promoted. However, additional studies with other fluorides and non-fluoride-containing solids will be required to establish this with certainty.

The novel compounds CF_3NBrCl and CF_3NBr_2 are pale yellow solids melting at −62.5 to −61.5 °C and −56.4 to −55.5 °C, respectively. They are thermally stable in the dark at 22 °C, but they readily decompose under the influence of Pyrex-filtered sunlight.

$$2CF_3NBrX \xrightarrow{\ h\nu\ } CF_3N\!=\!NCF_3 + 2BrX \quad (X = Cl,\ Br)$$

The compounds are readily identified by their MH^+ and M^+ molecular ions with the expected isotope ratios in the CI and EI mass spectra, by their ^{19}F NMR (internal $CFCl_3$) δ-(CF_3NBrCl) = −72.3 (s) and $\delta(CF_3NBr_2)$ = −70.5 (s), δ-(CF_3NCl_2) = −78, and by their characteristic IR spectra. The latter are very similar to those of CF_3NCl_2 except in the 850–650-cm^{-1} region where each show two characteristic strong absorptions (cm^{-1}): CF_3NCl_2, 812 and 708; CF_3NBrCl, 787 and 688; CF_3NBr_2, 758 and 675.

(9) BrCl is a very powerful chlorination reagent (more reactive than Cl_2) in the CsF-catalyzed reactions of R_fCN and R_fCF=NR_f: Zheng, Y.; DesMarteau, D. D., to be submitted for publication.

(10) This polyhalogen anion does not appear to be known, and this may indicate that Br_2F^- is not the active species in the reactions with −NClBr and −NCl$_2$. However, Br_2Cl^- is well characterized: Ault, B. S.; Andrews, L. *J. Chem. Phys.* 1976, 64, 4853.

(11) Cesium fluoride (99.9%) was activated by fusing it in a Pt dish, followed by grinding in a ball mill to a very fine powder under very anhydrous conditions. Potassium fluoride was similarly activated.

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(Perfluoroalkylimino)selenyl Chlorides

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Very few examples of compounds containing discrete nitrogen–selenium double bonds exist. The first of these was reported in 1967 and involved the preparation of ((arylsulfonyl)imino)selenyl chlorides.[2]

$$RSO_2NCl_2 + Se \rightarrow RSO_2N{=}SeCl_2 \quad (1)$$

Other examples such as $TeF_5N{=}SeCl_2$[3] and $SF_5N{=}SeCl_2$[4] have appeared only more recently.

$$TeF_5NH_2 + SeCl_4 \rightarrow TeF_5N{=}SeCl_2 + 2HCl \quad (2)$$

$$3SF_5NCl_2 + 2Se_2Cl_2 \rightarrow 3SF_5N{=}SeCl_2 + SeCl_4 \quad (3)$$

Both the arylsulfonyl and the pentafluorosulfanyl derivatives decompose upon standing in sharp contrast to the pentafluorotellurium compound. Thus, it was our interest to attempt the preparation of more $-N{=}Se<$ systems and to compare their stabilities to those of the above-mentioned compounds.

In order to prepare perfluoroalkyl analogues, one would envision either the free amines or the dichloroamines as starting materials. However, it is well documented that perfluoroalkylamines with fluorine in the α-position relative to the nitrogen readily eliminate HF to give the corresponding nitriles.[5] In fact this problem has[6] and can be circumvented by using the dichloramines as starting materials (see Scheme I). Our investigation has also led to a new one-step, high-yield synthesis of (trifluoromethyl)dichloramine.
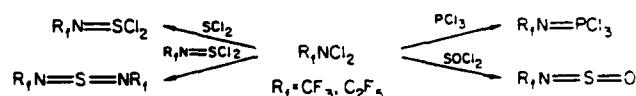
Experimental Section

Materials. ClF,[7] $C_2F_5NCl_2$,[8] and FC(O)NCl_2[9] were prepared by literature methods; BrCN, CF_3CN, Se, Se_2Cl_2, and H_2SeO_3 were obtained from commercial sources and used without further purification. *Caution!* Many N-halo compounds are known to be powerful explosives; therefore, suitable safety precautions should be kept in mind. We advise that the preparations and reactions of these materials be done on a small scale.

Spectra. Infrared spectra were obtained on a Perkin-Elmer 1430 Data System, while Raman spectra were taken on a Spex 1403 Ramalog double spectrophotometer with a Scamp data system. Mass spectra were obtained on a HP 5985A GC/MS system. The mass numbers are given for ^{80}Se and ^{35}Cl; the intensities include all isotopes. Fluorine-19 NMR spectra were recorded on a JEOL FX-90Q spectrometer at 84.25 MHz and referenced to internal CCl_3F. Selenium-77 NMR spectra were taken at 17.06 MHz and referenced to external H_2SeO_3.

Preparation of (Trifluoromethyl)dichloramine. Cyanogen bromide (10.0 mmol, 1.06 g) was condensed into the bottom of a 95-mL Monel cylinder chilled to liquid-nitrogen temperature. The level of the liquid nitrogen was then raised, and ClF (65 mmol) was added slowly so that it would condense into the upper portion of the cylinder. The reaction vessel was placed in a slush bath at –130 °C and allowed to warm slowly to room temperature overnight. The volatile materials were then transferred to the vacuum system and passed through a series of traps at –50, –125, and –196 °C. The trap at –50 °C stopped 1.14 g of a pale yellow solid with properties characteristic of BrF_3.[10] The contents of the –125 °C trap, consisting primarily of CF_3NCl_2 and Cl_2, were then shaken over mercury until complete removal of the Cl_2. Repeated distillation gave CF_3NCl_2 (9.5 mmol) in 95% yield, stopping in the trap at –125 °C.

Preparation of (Trifluoromethyl)imino)selenyl Dichloride. Method A. Diselenium dichloride (1.14 g, 5.0 mmol) was loaded into an FEP tube reactor with a metal valve in the drybox. After evacuation and cooling to –196 °C, approximately 10 mL of dry CCl_3F was condensed into the reactor. This mixture was warmed to room temperature and stirred to form a homogeneous solution before being refrozen in liquid nitrogen. An additional 1 mL of CCl_3F was then condensed in followed by 1.25 g of CF_3NCl_2 (8.1 mmol). The reaction mixture was placed in a –50 °C bath and maintained at the temperature overnight. Over the next 24-h period, the temperature of the bath was allowed to rise slowly to room temperature. During this time, a white precipitate formed and the color of the solution changed from dark red to light yellow. The volatile materials were then transferred to the vacuum line and passed through a series of traps at –15, –55, and –196 °C. The pale yellow, milky liquid that stopped in the trap at –55 °C was further purified by reaction with fresh CF_3NCl_2 for short periods of time between distillations. This process was repeated until the product was obtained as a clear liquid (1.55 g, 89% yield). The white solid (>0.45 g) was identified as $SeCl_4$ through its Raman spectrum.[11]

Method B. Selenium (0.47 g, 6.0 mmol) and CF_3NCl_2 (0.95 g, 6.2 mmol) were reacted under the same conditions as above. The 0.70 g of material stopping in the –55 °C trap was found to contain $CF_3N{=}SeCl_2$ along with other products ($CF_3N{=}NCF_3$, Se_2Cl_2).

$CF_3N{=}SeCl_2$: IR (gas) 1280 (w), 1237 (vs), 1200 (s), 1174 (s), 1038 (m), 771 (w), 651 (w), 610 (w) cm^{-1}; IR (liquid) 1220 (vs b), 1145 (vs b), 1024 (m), 962 (w), 764 (m), 650 (m), 609 (m), 515 (w) cm^{-1}. Raman (liquid) 1028.5 (6), 769 (23), 523? (6), 379 (59), 356.5 (100), 331 (52), 246 (25), 195 (27), 165 (44), 114 (17) cm^{-1}; mass spectrum (70 eV) m/z (relative intensity) 233 M$^+$ (3), 198 [M – Cl]$^+$ (100), 179 [M – Cl – F]$^+$ (20), 163 CF_3NSe^+ (25), 150 $SeCl_2^+$ (6), 144 CF_2NSe^+ (26), 115 $SeCl^+$ (19), 94 NSe^+ (34), 80 Se^+ (24); chemical ionization mass spectrum (methane) m/z (relative intensity) 234 [M + H]$^+$ (100), 214 [M – F]$^+$ (33), 199 [M + H, –Cl]$^+$ (10), 198 [M – Cl]$^+$ (24), 180 [M + H, –Cl – F]$^+$ (7), 179 [M – Cl – F]$^+$ (8), 150 $SeCl_2^+$ (7); ^{19}F NMR δ –50.6 (s, CF_3); ^{77}Se NMR δ 1073 (q, N=Se, $^3J_{Se-F} = 35$ Hz).

Decomposition of $CF_3N{=}SeCl_2$. Samples of $CF_3N{=}SeCl_2$ were observed to begin to decompose within 30 min at room temperature. At first, a white precipitate formed followed by a progressive reddening in color of the remaining liquid. A 1.53-g sample of $CF_3N{=}SeCl_2$ left standing in an FEP tube reactor for 9 days gave 0.33 g of $CF_3N{=}NCF_3$ (IR, NMR)[12] as the principal, volatile, decomposition product following reaction workup. Although not identified in this experiment (see below), the white solid and red liquid that formed were believed to be $SeCl_4$ and Se_2Cl_2, respectively.
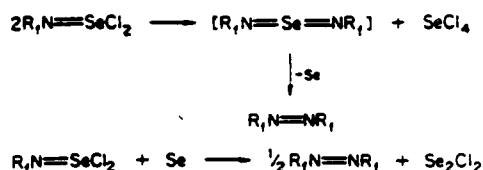
In a separate experiment $CF_3N{=}SeCl_2$ (0.16 g, 0.7 mmol) was hydrolyzed with H_2O (0.0270 g, 1.5 mmol). The volatile products, which were identified by infrared spectroscopy, included HCl, CO_2, and SiF_4.

Preparation of ((Pentafluoroethyl)imino)selenyl Dichloride. Diselenium dichloride (1.37 g, 6.0 mmol) and $C_2F_5NCl_2$ (2.12 g, 10.4

Scheme I

(1) Current address: Department of Chemistry, The University of Alabama, University, AL 35486.
(2) Bal'on, Ya. G.; Levchenko, E. S. *Zh. Org. Khim.* 1967, 3, 777; *Chem. Abstr.* 1967, 67, 43518a.
(3) Hartl, H.; Huppmann, P.; Lentz, D.; Seppelt, K. *Inorg. Chem.* 1983, 22, 2183.
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(5) (a) Klöter, G.; Lutz, W.; Seppelt, K.; Sundermeyer, W. *Angew. Chem.* 1977, 89, 754; *Angew. Chem., Int. Ed. Engl.* 1977, 16, 707. (b) Kumar, R. C.; Shreeve, J. M. *J. Am. Chem. Soc.* 1980, 102, 4958.
(6) (a) Leidinger, W.; Sundermeyer, W. *J. Fluorine Chem.* 1981/82, 19, 85. (b) Leidinger, W.; Sundermeyer, W. *Chem. Ber.* 1982, 115, 2892.
(7) Zheng, Y. Y.; DesMarteau, D. D. *J. Org. Chem.* 1983, 48, 444.
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(11) Hayward, G. C.; Hendra, P. J. *J. Chem. Soc. A* 1967, 643.
(12) Chambers, W. J.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* 1962, 84, 2337.
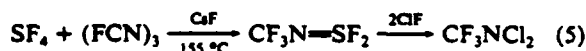
Scheme II

$$2R_fN{=\!=}SeCl_2 \longrightarrow [R_fN{=\!=}Se{=\!=}NR_f] + SeCl_4$$

$$\downarrow -Se$$

$$R_fN{=\!=}NR_f$$

$$R_fN{=\!=}SeCl_2 + Se \longrightarrow \tfrac{1}{2}R_fN{=\!=}NR_f + Se_2Cl_2$$

mmol) were reacted under the same conditions given in method A for $CF_3N{=\!=}SeCl_2$. The product $C_2F_5N{=\!=}SeCl_2$ (1.8i g, 6.8 mmol) was isolated as a clear, pale yellow liquid in 76% yield. IR (gas) 1233 (vs), 1212 (vs), 1134 (s), 1097 (vs), 929 (m), 754 (w), 704 (m) cm⁻¹; IR (liquid) 1203 (vs b), 1116 (m), 1084 (s), 933 (m), 753 (w), 704 (m) cm⁻¹; Raman (liquid) 933 (3), 755 (26), 704 (3), 373 (100), 367 (66), 360 (74), 331 (53), 314 (44), 265 (10), 168 (53), 142 (35) cm⁻¹; mass spectrum (70 eV) m/z (relative intensity) 248 [M – Cl]⁺ (61), 229 [M – Cl – F]⁺ (35), 214 [M – CF₃]⁺ (46), 213 $C_2F_5NSe^+$ (23), 194 $C_2F_4NSe^+$ (29), 179 [M – CF₃ – Cl]⁺ (27), 150 $SeCl_2^+$ (23), 115 $SeCl^+$ (100), 94 NSe^+ (20), 80 Se⁺ (34), 69 CF_3^+ (71), 50 CF_2^+ (7); chemical ionization mass spectrum (methane) m/z (relative intensity) 284 [M + H]⁺ (100), 264 [M – F]⁺ (71), 248 [M – Cl]⁺ (65), 214 [M – CF₃]⁺ (20); ¹⁹F NMR δ –86.1 (s, CF₃), –89.5 (s, CF₂); ⁷⁷Se NMR δ 1088 (t, N{=\!=}Se, $^3J_{Se-F}$ = 36.7 Hz).

Decomposition of $C_2F_5N{=\!=}SeCl_2$. The pentafluoroethyl derivative was found to decompose in a fashion similar to that of $CF_3N{=\!=}SeCl_2$. Analysis by Raman spectroscopy revealed that the white solid formed in the decomposition was $SeCl_4$.[11] A sample of $C_2F_5N{=\!=}SeCl_2$ (1.90 g, 7.0 mmol) left standing in an FEP tube reactor for 4 days gave $C_2F_5N{=\!=}N$-C_2F_5[12] (0.53 g, 2.0 mmol) as the principal, volatile, decomposition product. A small quantity of CF_3CN (<0.25 mmol) was also found in the product mixture.
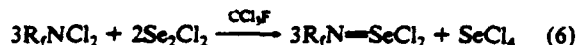
Results and Discussion

The reaction of BrCN with ClF gives a new, efficient method for producing (trifluoromethyl)dichloramine. Previously the best method of preparing CF_3NCl_2 relied on first preparing $CF_3N{=\!=}SF_2$ and then reacting this material with ClF.[9]

$$BrCN + 6ClF \rightarrow CF_3NCl_2 + 2Cl_2 + BrF_3 \qquad (4)$$

$$SF_4 + (FCN)_3 \xrightarrow[155\,°C]{CsF} CF_3N{=\!=}SF_2 \xrightarrow{2ClF} CF_3NCl_2 \qquad (5)$$

The yield in the BrCN reaction is substantially higher, but we have not attempted to scale this reaction beyond 10 mmol.

The dichloramines CF_3NCl_2 and $C_2F_5NCl_2$ react readily with Se_2Cl_2 to give the corresponding iminoselenyl dichlorides and $SeCl_4$.

$$3R_fNCl_2 + 2Se_2Cl_2 \xrightarrow{CCl_3F} 3R_fN{=\!=}SeCl_2 + SeCl_4 \qquad (6)$$

Both reactions proceed at a somewhat higher temperature than does that of the sulfur analogue $SF_5N{=\!=}SeCl_2$ and without the intermediate blackening (elemental Se?).[4] The trifluoromethyl derivative is also formed in the reaction of CF_3NCl_2 with elemental selenium; however, one cannot rule out the initial formation of Se_2Cl_2 in this reaction.

$$CF_3NCl_2 + Se \rightarrow CF_3N{=\!=}SeCl_2 \qquad (7)$$

Diselenium dichloride was also found to react with $FC(O)NCl_2$, but the reaction product was too unstable to be isolated and characterized.

The instability of the (perfluoroalkylimino)selenyl halides is not totally unexpected. It is surprising that the major products of the decomposition are not analogous to those observed in the decomposition of $SF_5N{=\!=}SeCl_2$.[4] Only a small quantity of CF_3CN observed in the decomposition of $C_2F_5N{=\!=}SeCl_2$ gave evidence for an analogous pathway.

$$2SF_5N{=\!=}SeCl_2 \rightarrow 2SF_3{\equiv\!=}N + SeCl_4 + SeF_4 \qquad (8)$$

$$2C_2F_5N{=\!=}SeCl_2 \rightarrow 2CF_3C{\equiv\!=}N + SeCl_4 + SeF_4 \qquad (9)$$

Other evidence indicates that the major decomposition reaction is that shown in eq 10. A possible mechanism for this decom-

$$6R_fN{=\!=}SeCl_2 \rightarrow 3R_fN{=\!=}NR_f + 2SeCl_4 + 2Se_2Cl_2 \qquad (10)$$

position is shown in Scheme II. This mechanism is supported by the early appearance of $SeCl_4$ in the decomposition and by the fact that both $CF_3N{=\!=}SeCl_2$ and $C_2F_5N{=\!=}SeCl_2$ react with elemental selenium to give the respective perfluoroazoalkane and a heavy, red liquid believed to be Se_2Cl_2. Sharpless and co-workers have also previously proposed selenium diimides as reactive intermediates in organic syntheses.[13]

The Raman stretching frequencies at 1028.5 cm⁻¹ in $CF_3N{=\!=}SeCl_2$ and at 933 cm⁻¹ in $C_2F_5N{=\!=}SeCl_2$ have been assigned to the N{=\!=}Se stretch. A similar, unexpectedly large difference in the N{=\!=}Se stretching frequencies of $SF_5N{=\!=}SeCl_2$ and TeF_5-$N{=\!=}SeCl_2$ (~80 cm⁻¹) has previously been observed.[4] A possible explanation for this variation could be the degree of association and/or association mechanism in these compounds.[14] The selenium-77 NMR spectra reported herein are consistent with Se(IV) species, and the observed couplings to fluorine strongly support the identity of the new compounds.

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Some reactions of highly halogenated
N-bromo-1-fluoro-1-alkanimines

by

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Cycloaddition and Oxygen-Transfer Reactions of 2-(Trifluoromethyl)-3,3-difluorooxaziridine[1]

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The oxaziridine CF_3NCF_2O (1) cycloadds to various 1,1-difluoroolefins under mild conditions, forming perhalo-1,3-oxazolidines, and to dialkyl ketones, forming the corresponding 1,3,4-dioxazolidines. Reaction of 1 with trimethylsilyl cyanide results in the formation of $(CH_3)_3SiN=C=NCF_3$ and COF_2, but 1 is unreactive with other alkyl nitriles and isocyanides. With 2,5-dimethylfuran and 2,3-dimethylbutene, 1 reacts rapidly and under mild conditions (~-50 °C) to yield $CF_3N=CF_2$ and organic products derived from the transfer of a single oxygen atom.

Our studies of the unusual oxaziridine pentafluoroazapropene oxide (PFAPO), CF_3NCF_2O (1), have shown thus far that its reaction chemistry is similar in some ways to that of hexafluoropropene oxide (HFPO), $CF_3CFC\overline{F_2O}$.[2,3] Both compounds readily undergo ring opening by nucleophiles, with attack exclusively at the central nitrogen or carbon, respectively. Hexafluoropropene oxide is, however, generally unreactive toward unsaturated systems; cycloaddition reactions of this epoxide with olefins have not been reported and only a single cycloadduct with acetone has been reported.[4,5] Pentafluoroazapropene oxide in contrast, readily reacts with a number of 1,1-difluoroolefins to form 3-(trifluoromethyl)perhalo-1,3-oxazolidines and reacts readily with certain ketones to form 2,2-disubstituted 5,5-difluoro-4-(trifluoromethyl)-1,3,4-dioxazolidines.

Additional differences in reactivity between HFPO and PFAPO are indicated by the isomerization of HFPO to hexafluoroacetone with SbF_5,[3] whereas PFAPO forms a high percentage of a dimer along with small amounts of higher oligomers.[2b] Finally, in this work we report the facile oxygen atom-transfer reaction of PFAPO with electron-rich alkenes, a reaction not observed with HFPO.

Experimental Section

General Methods. All work was carried out in Pyrex or stainless steel (types 304 and 316) vacuum systems equipped with glass-Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements. Temperatures were measured by using a digital-indicating iron–constantan thermocouple.

Infrared spectra were recorded with a Perkin-Elmer 337, 1330, 180, or 1430 spectrometer using a 10-cm glass cell fitted with AgCl or KCl windows. NMR spectra were recorded with a Varian XL-100-15 spectrometer by using ~80 mol % $CFCl_3$ as a solvent and an internal reference or with a JEOL FX-90Q spectrometer by using various deuteriated media as both solvent and internal lock and ~1% $CFCl_3$ as the internal reference. Hydrogen chemical shifts are reported relative to internal $(CH_3)_4Si$.

Mass spectra were recorded with either a Finnigan 4021-C or a Hewlett-Packard 5985B instrument at 70 eV for electron-impact (EI) and chemical ionization [CI,CH_4] spectra. Samples were introduced by direct gas injection.

Melting points were determined by a modified Stock procedure. Vapor pressures as a function of temperature were determined by using a small isoteniscope.[6] Equations describing pressure as a function of temperature were obtained by a least-squares fit of the data to both linear and quadratic equations, and the best fit is reported.

For further purification of reaction products, GLC was carried out with a Victoreen Series 4000 gas chromatograph equipped for gas injection, TCD, and low-temperature collection. Columns of 10, 2, or 1 ft × $^3/_8$ in. packed with 35% Halocarbon 11-21 polymer oil on acid-washed Chromosorb P were used.

Reagents. The olefins were commercially available and were used as received. Other organic reactants were purified by distillation under vacuum. Oxaziridine 1 was prepared as described previously.[7]

General Procedure for Reaction of Oxaziridine 1 with Olefins. To a ~100-mL Pyrex vessel fitted with a glass-Teflon valve were added 1 (1–3 mmol) and an equimolar amount of olefin by vacuum transfer. The mixture was then heated at 55–100 °C for ~18 h, unless otherwise noted. The products were separated by vacuum fractionation through a series of cold traps, followed by GLC as needed.

(a) With $CF_2=CF_2$. Perfluoro-3-methyloxazolidine (2a) was obtained in 60% yield; bp 21 °C; log P (torr) = 6.969 − (949.14/T) − (74200/T^2); ΔH_{vap} = 6.65 kcal/mol; ΔS_{vap} = 22.6 eu; IR (gas) 1415 (m), 1360 (s), 1325 (vs), 1245 (vs), 1165 (m), 1080 (m), 1010 (m), 960 (vw), 910 (m), 745 (w), 700 (w), 680 (w), 580 (w) cm⁻¹; MS (CI, major), m/z 250 [(M + 1)⁺], 230 [(M + 1 − HF)⁺], 200 [(M + 1 − CF_2)⁺], 183 ($C_3F_7N^+$), 154, 152, 134 ($C_2HF_5N^+$), 114; MS (EI, major), m/z (relative intensity) 249 (M⁺), 230 [(M − F)⁺, 100], 199 [(M − CF_2)⁺], 183 [(M − COF_2)⁺], 180, 164 ($C_3F_6N^+$),

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153, 142 ($C_3F_4NO^+$), 134, 133, 131, 130, 119, 116 ($C_2F_4NO^+$, 100), 114 ($C_2F_4N^+$), 100, 99, 97, 95, 92, 69 (CF_3^+), 65, 50 (CF_2^+), 47, 44;

^{19}F NMR ($CF_3{}^ANCF_2{}^BOCF_2{}^CCF_2{}^D$) ($CFCl_3$) δ A −57.5, B −58.2, C −86.5, D −93.3 (J_{AB} = 6.8, J_{BC} = 3.4, J_{AC} ≃ 1.5, J_{AD} = 6.8, J_{BD} = 6.8 Hz).

(b) With CF_2=CFCl. 4-Chloro-3-(trifluoromethyl)perfluorooxazolidine (2b) was obtained in 78% yield: bp 51 °C; log P (torr) = 6.230 − (717.6/T) − (119500/T^2); ΔH_{vap} = 6.66 kcal/mol; ΔS_{vap} = 20.5 eu; IR (gas) 1430 (vw), 1370 (m), 1315 (vs), 1245 (vs), 1185 (m), 1145 (m), 1095 (m), 1075 (m), 1025 (m), 945 (m), 870 (m), 785 (vw), 740 (m), 695 (vw), 620 (vw) cm^{-1}; MS (CI, major) m/z (relative intensity) 266 [(M + 1)$^+$, weak], 248/246 [(M + 1 − HF)$^+$, 100], 230 [(M + 1 − HCl)$^+$], 134 ($C_2HF_5N^+$); MS (EI, major), m/z (relative intensity) 230 [(M − Cl$^+$)], 182/180 [(M − CF$_3$O)$^+$], 164 ($C_3F_6N^+$), 132/130 ($C_2ClF_3N^+$), 116 ($C_2F_4O^+$), 114 ($C_2F_4N^+$), 113, 95, 87, 85, 76, 69 (CF_3^+, 100), 66, 50 (CF_2^+), 47;

^{19}F NMR ($CF_3{}^ANCF^BF^COCF^DF^ECF^FCl$) ($CFCl_3$) δ A −56.5, B −57.4, C −60.9, D −76.7, E −88.0, F −76.1 (J_{AB} = J_{AC} = J_{AF} = 7, J_{BC} = 93, J_{DE} = 111, $J_{BD \text{ or } BE}$ = $J_{CE \text{ or } CD}$ = 6.5, J_{EF} ≈ 5.5, J_{BF} ≈ 5.5 Hz).

(c) With CF_2=CFBr. 4-Bromo-3-(trifluoromethyl)perfluorooxazolidine (2c) was obtained in 85% yield: bp 65 °C; log P (torr) = 7.622 − (1604.8/T); ΔH_{vap} = 7.34 kcal/mol; ΔS_{vap} = 21.7 eu; IR (gas) 1420 (vw), 1400 (w), 1365 (vs), 1290 (vs), 1210 (vs), 1185 (m), 1145 (m), 1115 (w), 1090 (m), 1065 (m), 1020 (m), 920 (m), 855 (m), 740 (m), 695 (vw), 620 (vw); MS (CI, major), m/z (relative intensity) 292/290 [(M + 1 − HF)$^+$, 100], 230 [(M + 1 − HBr)$^+$], 211 ($C_4F_7NO^+$), 134 ($C_2HF_5N^+$); MS (EI, major), m/z (relative intensity) 230 [(M − Br)$^+$], 226, 224, 174, 164 ($C_3F_6N^+$), 160, 159, 131/129 ($CBrF_2^+$), 113 ($C_2F_4N^+$), 94, 91, 81/79 (Br$^+$), 76, 69 (CF_3^+, 100), 50 (CF_2^+), 47; ^{19}F NMR ($CF_3{}^ANCF^BF^COCF^DF^ECF^FBr$) ($CFCl_3$) δ A −56.4, B −56.1, C −59.6, D −71.6, E −87.9, F −71.5 (J_{AB} = J_{AC} = J_{AF} ≈ 7.8, J_{BC} = 96, J_{DE} = 125, J_{BD} ≈ 5, J_{CD} ≈ 4.5 Hz).

(d) With CF_2=CCl$_2$. 4,4-Dichloro-3-(trifluoromethyl)perfluorooxazolidine (2d) was obtained in 81% yield: vapor pressure [torr (°C)] 46.2 (9.8), 99.9 (26.2), 124.7 (31.8); IR (gas) 1410 (vw), 1390 (w), 1350 (s), 1295 (vs), 1255 (s), 1205 (vs), 1165 (m), 1130 (m), 1020 (m), 930 (w), 865 (m), 830 (m), 765 (vw), 730 (m), 605 (vw), 585 (vw), 540 (vw) cm^{-1}; MS (CI, major), m/z (relative intensity) 284/282 [(M + 1)$^+$, weak], 266/264/262 [(M + 1 − HF)$^+$], 248/246 [(M + 1 − HCl)$^+$, 100], 229, 228, 227, 149 ($C_2F_5NO^+$); MS (EI, major), m/z (relative intensity) 248/246 [(M − Cl)$^+$], 198, 196, 182/180 ($C_3ClF_3N^+$), 148, 146, 145, 134, 132, 130, 114, 113, 111, 103, 100, 87/85 (CF_2Cl^+), 82, 76, 69 (CF_3^+, 100), 66, 50(CF_2^+), 47; ^{19}F NMR ($CF_3{}^ANCF_2{}^BOCF_2{}^CCCl_2$) ($CFCl_3$) δ A −56.1, B −58.1, C −79.6 (J_{AB} = 7.7, J_{BC} = 3 Hz).

(e) With CF_2=CFCF=CF$_2$. 3-(Trifluoromethyl)-4-(trifluorovinyl)perfluoro-1,3-oxazolidine (2e) was obtained in 71% yield: glass, flows ~−105 °C; IR (gas) 1785 (s, CF=CF$_2$), 1370 (vs), 1345 (vs), 1300 (vs), 1265 (vs), 1220 (vs), 1165 (vs), 1125 (m), 1080 (s), 1020 (s), 935 (s), 885 (w), 870 (s), 800 (w), 745 (s), 700 (w), 665 (w), 625 (w), 585 (w), 555 (w), 495 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 312 (MH$^+$, weak), 311 (M$^+$), 293 [(M + 1 − HF)$^+$, 100], 292, 226, 176 ($C_4F_6N^+$), 157 ($C_4F_5N^+$), 69 (CF_3^+); MS (EI, major) m/z (relative intensity) 311 (M$^+$), 245 [(M − COF$_2$)$^+$], 226, 195, 181, 178 ($C_4F_6O^+$), 177, 176 ($C_4F_6N^+$, 100), 159 ($C_4F_5N^+$), 131, 116, 114, 112, 109, 69 (CF_3^+); ^{19}F NMR (380 MHz) [$CF_3{}^ANCF^BF^{B'}OCF^CF^CCF^D(CF^E$=$CF^FF^G)$] (20:80 CDCl$_3$/CCl$_4$) δ A −57.04, B −57.40, B′ −57.88, C −77.69, C′ −88.87, D −134, E −182, F −87.04, G (trans to E) −105 ($J_{BB'}$ = 93, J_{CC} = 134, J_{DF} = 42, J_{EG} = 115, J_{FG} = 55 Hz, others not readily determined).

(f) With CF_2=CHF. 2,2,4,4,5-Pentafluoro-3-(trifluoromethyl)-1,3-oxazolidine and 2,2,4,5,5-pentafluoro-3-(trifluoromethyl)-1,3-oxazolidine (3a and 3b) were formed in a ca. 40:60 ratio, in 33% yield: IR (gas) 3335 (w), 3025 (w), 1770 (w), 1410 (m), 1345 (vs), 1285 (s), 1215 (vs), 1140 (s), 1110 (s), 1075 (m), 1010 (s), 985 (m), 905 (m), 825 (m), 790 (m), 685 (w), 620 (w), 575 (w), 475 (w) cm^{-1}; M$_r$ calcd 231, found 222; ^{19}F NMR $CF_3{}^A$-$NCF^BF^COCH^XF^MCF^DF^E$ (major isomer, C_6D_6) δ A −57.2, B, C −51.3, −60.8, D, E −84.2, −100.4, M −132.2, X 5.02 (overlaps X of minor isomer) (J_{BC} = 98, J_{DE} = 180, J_{MX} = 60 Hz); ^{19}F NMR

$CF_3{}^ANCF^BF^COCF^DF^ECH^XF^M$ (minor isomer) δ A −57.8, B, C ~−55.6, ~−57 (overlaps F^A of major isomer), D, E −75.8, −92.4, M −144.8, X 4.92 (J_{BC} = 62, J_{DE} = 140, J_{MX} = 68 Hz).

(g) With CF_2=CBr$_2$. 4,4-Dibromo-3-(trifluoromethyl)perfluoro-1,3-oxazolidine (2f) was obtained in 25% yield: IR (gas) 1415 (vw), 1385 (vw), 1350 (s), 1295 (vs), 1250 (s), 1210 (vs), 1190 (s), 1160 (m), 1120 (m), 1090 (vw), 1020 (m), 905 (w), 835 (m), 790 (m), 755 (w), 725 (m), 655 (vw) 605 (vw), 580 (vw), 525 (vw) cm^{-1}; MS (CI, major), m/z (relative intensity) 353/351/347 [(M + 1 − HF)$^+$], 292/290 [(M − Br)$^+$, 100], 286, 241, 239, 226, 224, 134; MS (EI, major), m/z (relative intensity) 291/289 [(M − Br)$^+$], 226, 223, 190, 159/157 ($C_2BrF_2O^+$), 145, 131/129 ($CBrF_2^+$), 115, 113, 111, 109, 91, 85, 76, 69 (CF_3^+, 100); ^{19}F NMR ($CF_3{}^A$-$NCF_2{}^BOCF_2{}^CCBr_2$) ($CFCl_3$) δ A −56.2, B −58.1, C −75.8 (J_{AB} ≈ 8, J_{BC} = 2.8 Hz). Dibromofluoroacetyl fluoride was isolated in ~70% yield: IR (gas) 1875 (s), 1210 (s), 1120 (s), 1025 (m), 930 (w), 915 (m), 820 (m), 685 (w), 640 (w), 625 (w) cm^{-1}; MS (EI, major) m/z (relative intensity) 240/238/236 (M$^+$), 193/191/189 (CBr_2F^+), 159/157 [(M − Br)$^+$, 100], 131/129 ($CBrF_2^+$); ^{19}F NMR ($CBr_2F^ACOF^X$) ($CFCl_3$) δ A −66.6, X 7.40 (J_{AX} = 18 Hz). When 1 and CF_2=CBr$_2$ were allowed to react at ~23 °C for 18 h, only CBr$_2$FCOF and CF_3N=CF$_2$ were isolated.

(h) With CF_2=CH$_2$. A clear, nonvolatile oil was obtained: MS (EI, major) m/z 570, 429, 407, 357, 341, 321, 291; ^{19}F NMR (acetone/CFCl$_3$) δ −56.3 (br m, 5 F, CF_3NCF_2), −77.0 (br, 2 F, CF_2CH_2); ^1H NMR (acetic acid-d_6/acetone) δ 4.0 (br t, CF_2CH_2, J_{HF} = 9 Hz).

(i) With CF_3CF=CF$_2$. The reaction mixture was heated at 150 °C for 18 h. A clear, nonvolatile oil and a trace of volatile oxazolidine were obtained: IR (gas) 1380 (s), 1295 (vs), 1220 (vs), 1175 (s), 1140 (m), 1120 (m), 1095 (w), 1030 (m), 1005 (w), 970 (m), 895 (m), 870 (w), 755 (vw), 730 (m), 625 (vw), 580 (vw); MS (CI, major), m/z (relative intensity) 300 [(M + 1)$^+$], 281 [(MH − F)$^+$], 280 [(M − F)$^+$, 100], 230 [(M − CF$_3$)$^+$], 214 ($C_4F_8N^+$), 164 ($C_3F_6N^+$), 114 ($C_2F_4N^+$), 100, 95, 76, 69 (CF_3^+, 100), 50 (CF_2^+), 47; ^{19}F NMR, ($CF_3{}^ANCF^BF^{B'}OCF^CF^CCF^DCF_3{}^E$) ($CFCl_3$) δ A −56.1, B and B′ −57.5, C −79.3, C′ −86.8, D −139.9, E −76.9 (J_{AB} ≈ $J_{AB'}$ ≈ J_{AD} ≈ J_{AE} ≈ 8, $J_{CC'}$ = 135 Hz, other values not readily determined).

Reactions of 1 with Ketones. In a typical preparation, 1.0 mmol each of 1 and the ketone was condensed into a ~140-mL Pyrex vessel and left at ~23 °C for 18 h. Trap-to-trap fractionation, followed by GLC purification, afforded the 2,2-disubstituted 5,5-difluoro-4-(trifluoromethyl)dioxazolidine.

(a) With Acetone. 5,5-Difluoro-2,2-dimethyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (4a) was obtained in 75% yield: IR (gas) 3010 (w), 2950 (w), 1865 (impurity, m), 1460 (w), 1385 (m), 1290 (vs), 1210 (vs), 1150 (m), 1110 (m), 1030 (s), 1005 (m), 975 (m), 905 (m), 875 (w), 830 (w), 760 (w), 690 (w), 640 (w), 550 (w), 525 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 208 (MH$^+$), 207, 189, 188 [(M + 1 − HF)$^+$, 100], 182, 178, 170, 150 ($C_2HF_5NO^+$), 143, 142 [(M + 1 − COF$_2$)$^+$], 141, 124, 123, 122 ($C_4H_6F_2NO^+$), 112; MS (EI, major), m/z (relative intensity) 207 (M$^+$), 192 [(M − CH$_3$)$^+$], 188 [(M − HF)$^+$], 150 ($C_2HF_5NO^+$), 149, 142, 141 [(M − COF$_2$)$^+$], 122 ($C_4H_6FNO^+$), 85, 69 (CF_3^+), 61, 58, 57, 47, 43 (100), 42, 41, 40, 39; ^{19}F and ^1H NMR see ref 2b.

(b) With 2-Butanone. 5,5-Difluoro-2-methyl-2-ethyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (4b) was obtained in 35% yield: mp −108 to −107 °C; IR (gas) 2990 (m), 2955 (w), 2900 (w), 2430 (w), 1465 (w), 1390 (w), 1310 (vs), 1285 (vs), 1215 (vs), 1180 (m), 1150 (m), 1120 (m), 1040 (s), 995 (m), 945 (m), 915 (m), 820 (w), 770 (w), 720 (w), 690 (w), 645 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 222 [(M + 1)$^+$], 221, 203, 202 [(M + 1 − HF), 100], 192, 178, 156 [(M + 1 − COF$_2$)$^+$], 155, 150 ($C_2HF_5NO^+$), 137, 136 ($C_2HF_5O^+$), 137, 136 ($C_2HF_5O^+$), 112, 73 ($C_4H_9O^+$), 72, 69 (CF_3^+), 57, 55; MS (EI, major), m/z (relative intensity) 221 (M$^+$), 206 [(M − CH$_3$)$^+$], 192 [(M − C$_2$H$_5$)$^+$], 172, 155, 150 ($C_2HF_5NO^+$, 100), 149, 72, 69, 57, 55; ^{19}F NMR [$CF_3{}^ANCF_2{}^BOC(CH_3)(C_2H_5)O$] (acetone-$d_6$) δ A −68.14, B −67.35 ($J_{AB}$ ≈ 7 Hz); ^1H NMR [$CF_3NCF_2OC(CH_3{}^A)(CH_2{}^BCH_3{}^C)O$] (acetone-$d_6$) δ A 1.71, B 2.03, C 1.02 (J_{BC} = 15 Hz).

(c) With 3,3-Dimethyl-2-butanone. 5,5-Difluoro-2-methyl-2-*tert*-butyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (4c) was obtained in 40% yield: mp −94 °C; IR (gas) 3010 (w), 2980 (m), 2925

(w), 2890 (w), 1485 (w), 1385 (m), 1310 (vs), 1280 (s), 1250 (s), 1225 (s), 1205 (s), 1160 (s), 1145 (s), 1080 (m), 1035 (m), 995 (m), 950 (m), 920 (w), 845 (w), 690 (w), 670 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 250 [(M + 1)$^+$], 231, 230 [(M + 1 – HF)$^+$], 202, 192 [(M – C$_4$H$_9$)$^+$], 184 [(M + 1 – COF$_2$)$^+$], 165, 164 (C$_7$H$_{12}$F$_2$NO$^+$), 150, 136, 103, 102, 101 (C$_6$H$_{13}$O$^+$), 100, 84 (CF$_3$N$^+$, 100), 83, 69 (CF$_3$$^+$), 57; MS (EI, major), m/z (relative intensity) 249 (M$^+$, weak) 19? [(M – C$_4$H$_9$)$^+$], 172, 150 (C$_2$HF$_5$NO$^+$), 100, 85, 84, 83 (CF$_3$N$^+$), 69 (CF$_3$$^+$), 58, 57, (C$_4H_9$$^+$, 100), 55; ^{19}F NMR (CF$_3$^{A}NCF$_2$^{B}OC[CH$_3$][C(CH$_3$)$_3$]O) (benzene-d_6) complex A$_3$B$_2$ pattern, most intense peak δ –68.31; ^{1}H NMR (CF$_3$NCF$_2$OC-[CH$_3$^{A}][C(CH$_3$)$_3$^{B}]O) (benzene-d_6) δ A 1.26, B 0.77.

(d) **With 3-Buten-2-one.** 5,5-Difluoro-2-methyl-2-vinyl-4-(trifluoromethyl)-1,3,4-dioxazolidine (4d) was obtained in 52% yield: bp (extrapolated, ~60 °C dec) 95 °C; log P (torr) = 6.7997 – (1078.1/T) – (135017/T^2); ΔH_{vap} = 82.85 kcal/mol; ΔS_{vap} = 22.5 eu; IR (gas) 3110 (w), 3040 (w), 3010 (w), 2950 (w), 1450 (m), 1420 (m), 1385 (m), 1295 (vs), 1220 (vs), 1150 (vs), 1100 (m), 1030 (s), 995 (s), 950 (s), 920 (m), 825 (w), 775 (w), 700 (w), 660 (w), 630 (w) cm^{-1}; MS (CI, major), m/z (relative intensity) 220 [(M + 1)$^+$], 201 [(M – F)$^+$], 200 [(M + 1 – HF)$^+$, 100], 178, 154 [(M + 1 – COF$_2$)], 153, 152, 150, 134 (C$_5$H$_6$F$_2$NO$^+$), 71 (C$_4$H$_7$O$^+$); MS (EI, major), m/z (relative intensity) 219 (M$^+$), 204 [(M – CH$_3$)$^+$], 192 [(M – C$_2$H$_3$)$^+$], 153, 152 (100), 150, 149, 70, 69 (CF$_3$$^+$), 55, 54, 53; ^{19}F NMR [CF$_3$^{A}NCF$_2$^{B}O(CH$_3$)(CH=CH$_2$)O] (20:80 CDCl$_3$/CCl$_4$) complex A$_3$B$_2$ pattern, most intense peak δ –68.98; ^{1}H NMR [CF$_3$NCF$_2$OC(CH$_3$^{A})(CH^L=CH^{M}H^N)O] (20:80 CDCl$_3$/CCl$_4$) δ A 1.76, L (trans to N) 5.78, M 5.46, N ~6.0 (J_{LM} ≈ 1.5, J_{LN} ≈ J_{MN} ≈ 10 Hz).

Reactions of 1 with 2,5-Dimethylfuran and 2,3-Dimethylbutene. In each case, 1.0 mmol each of 1 and the organic coreactant was condensed (–196 °C) into a ~140-mL Pyrex vessel having a 10-mm NMR tube attached to its neck. The region of the vessel containing the reactants was then immersed in an ethanol bath held at ~–50 to –40 °C. At the end of the reaction period (~15 min for 2,5-dimethylfuran, ~1 h for 2,3-dimethylbutene) volatile materials were pumped out (at –40 °C for 2,5-dimethylfuran, –100 °C for 2,3-dimethylbutene) into a –196 °C trap. The volatile materials were shown by IR to consist primarily of CF$_3$N=CF$_2$, traces of unreactive impurities from preparation of 1, and a small amount of unreacted 1. The reactor was then cooled to –196 °C, and sufficient C$_6$D$_6$ to make a ~1 M NMR sample was condensed in, along with (CH$_3$)$_4$Si as an internal standard. The sample was rapidly melted and poured into the attached NMR tube, which was then cooled to –196 °C and sealed under vacuum. The samples were stored at –196 °C until immediately before acquiring the NMR spectra.

NMR of materials from oxidation of 2,3-dimethylbutene: ^{1}H (C$_6$D$_6$) δ 1.11 (s, tetramethyloxirane); ^{13}C δ 21.15, 61.46 (tetramethyloxirane) [lit.[8] δ 21.2, 61.7 (61.2)]. No absorptions attributable to 2,3-dimethylbutene were seen.
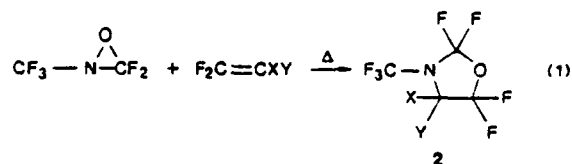
NMR of materials from oxidation of 2,5-dimethylfuran: ^{1}H (C$_6$D$_6$) δ 5.70, 1.87 (large s, cis-3-hexene-2,5-dione), δ 5.77, 2.06 (small s, 2,5-dimethylfuran), 1.42, 1.33; ^{13}C (C$_6$D$_6$) δ 199.8 (carbonyl), 29.25 (methyl), 135.5 (olefin) [attributable to cis-3-hexene-2,5-dione], 13.44, 106.5, 150.3 [attributable to 2,5-dimethylfuran]. No other ^{13}C signals were observed initially. An overnight run, however, led to extensive decomposition as seen both by spectral changes and darkening of the sample.

In a separate experiment, 1.0 mmol each of 1 and 2,5-dimethylfuran was condensed into a ~140-mL Pyrex vessel and allowed to react as described above. After pumping off the CF$_3$N=CF$_2$, the yellowish/greenish/white largely crystalline material remaining in the flask was allowed to warm to room temperature. It turned red immediately upon melting. The infrared spectrum (liquid film) indicated that the oxidation product was cis-3-hexene-2,5-dione: 1685 (s, C=O), 1613 (s, cis-alkene) cm^{-1} [lit.[9] 1689, 1613 cm^{-1}]. A broad hydroxyl absorption was also seen. We attribute this to water, as the dione

is known to be highly hygroscopic.[9] The material remaining in the flask decomposed to a black sludge overnight.
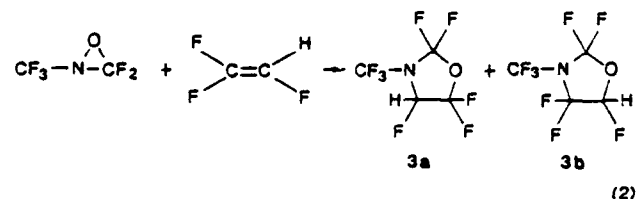
Results and Discussion

Cycloadditions with Olefins. Oxaziridine 1 reacts readily and regiospecifically with a number of simple 1,1-difluoroolefins under mild conditions (50–100 °C) to afford good yields of the corresponding 3-(trifluoromethyl)perhalo-1,3-oxazolidines 2 (eq 1).

$$CF_3 - N \overset{O}{\overset{/\backslash}{\underset{}{}}} CF_2 \ + \ F_2C = CXY \ \overset{\Delta}{\longrightarrow} \ F_3C - N \quad (1)$$

2a. X=Y=F; **b.** X=F,Y=Cl; **c.** X=F, Y=Br; **d.** X=Y=Cl; **e.** X=F, Y=CFCF$_2$; **f.** X=Y=Br
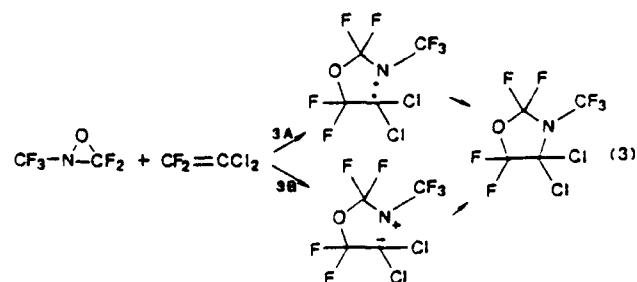
The nature of the reactivity of olefins with 1 begins to change when the olefin is substituted with hydrogen or trifluoromethyl. While 1 cycloadds readily to CF$_2$=CHF, the yield is poor, and much less regioselectivity is seen: a 40:60 mixture of 3a and 3b is obtained (eq 2). Reactions

$$(2)$$

of 1 with CF$_2$=CH$_2$, CFH=CFH (mixtures of cis and trans isomers), and CF$_3$CF=CF$_2$ afforded nonvolatile oils which may be copolymers of the olefins and the oxaziridine, since both of the starting materials are consumed. [In the reaction with CF$_3$CF=CF$_2$, a trace of oxazolidine (reaction 1, X = F, Y = CF$_3$) was obtained.]

Attempts to carry out the cycloaddition of 1 with C$_2$H$_4$, CFCl=CFCl, perfluorocyclopentene, perfluoro-2-butyne, acrylonitrile, and acetylene (with which no reaction was observed even at 150 °C) failed; the starting materials were recovered in each case.

To account for the reactivity of 1 with the above olefins, we propose that the [2 + 3] cycloadditions, involving ring opening via the nitrogen–oxygen bond, could occur in two ways: a biradical mechanism in which the products are determined by the relative stabilities of the intermediate radicals or by formation of a 1,3-dipolar species CF$_3$N$^+$-CF$_2$O$^-$, where the products are controlled by the nucleophilic attack of the oxygen of the 1,3-dipolar species on the alkene. Either route can serve to explain the observed regiospecificity of the additions and both are consistent with the relative reactivity of the olefins. These proposals are illustrated in eq 3 for CF$_2$=CCl$_2$.

$$(3)$$

Reaction path 3A is supported, in part, by analogy to the well-known [2 + 2] thermal cycloadditions of 1,1-difluoroolefins which are generally accepted as proceeding

(8) (a) Paulson, D. R.; Tang, F. Y. N.; Moran, G. F.; Murray, A. S.; Pelka, B. P.; Vasquez, E. M. *J. Org. Chem.* **1975**, *40*, 184. (b) Davies, S. G.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 861.
(9) Levisalles, J. *Bull. Soc. Chim. Fr.* **1957**, 997.

via a biradical transition state.[10] In this case, the more nucleophilic and less hindered oxygen of 1 attacks the 1,1-difluoromethylene carbon of the olefin to give the most stable intermediate biradical. The similarity of this process to that of the [2 + 2] cycloadditions of fluoroolefins is reinforced by the fact that a 1,1-difluoroolefin reactant is rigorously required in both cases. Reaction path 3B, while consistent with the expected nucleophilic attack on C-F_2=CCl_2, is disfavored by the fact that examples of 1,3-dipolar additions to fluoroolefins leading to five-membered rings are rare. A more definitive resolution of this interesting mechanistic question must await further work.

The perhalooxazolidines 2 are stable compounds of low reactivity (with the exception of 2e, which contains a reactive trifluorovinyl group). No decomposition of compounds 2a–f was noted during handling in glass or stainless steel vacuum systems or in contact with mercury at room temperature. The low reactivity of 2a, prepared by another method, has been reported previously.[11] In addition to the reagents reported in ref 11, we have found 2a to be unreactive with CsF, chromic acid, and $KMnO_4$ in water/tert-butyl alcohol. Compound 2a was recovered unchanged upon heating alone at 110 °C or with CsF at 60 °C.

The assigned structures of the oxazolidines were strongly supported by their ^{19}F NMR spectra. The two doublets of a typical AB pattern arising from the methylene fluorines at both C-2 and C-5 of oxazolidines 2b and 2c clearly demonstrate the magnetic nonequivalence of each member of each of the pairs; this nonequivalence is induced by the chiral center at C-4 in 2b and 2c. Similarly, the spectra of 3a and 3b are complicated by the chiral center at C-4 and C-5, respectively. The ^{19}F spectrum of 2a agrees with that reported earlier.[11]

Oxazolidine 2e gave rise to a highly complex 90-MHz ^{19}F NMR spectrum, as all eight of the ring and olefinic fluorines are magnetically nonequivalent, and extensive coupling of the ring fluorines both with each other and with the olefinic fluorines was observed. The spectrum was simplified considerably when obtained at 380 MHz.[12]

Oxygen Atom Transfer. The reaction of 1 with hydrocarbon olefins other than ethylene reveals a striking new reaction path: instead of forming a cycloadduct, 1 transfers its oxygen atom to the olefin, forming CF_3N=CF_2.

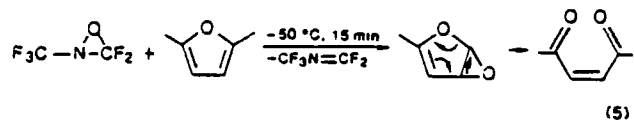This process is illustrated in eq 4 for 2,3-dimethylbutene, which gives tetramethyloxirane as the sole oxidation product.

$$F_3C-\overset{\overset{O}{\|}}{N}-CF_2 \; + \; \underset{}{\text{>=<}} \; \xrightarrow[\sim 1h]{-50\,°C} \; \overset{O}{\underset{}{\triangle}} \; + \; CF_3N\!=\!CF_2 \quad (4)$$

Similar reactions have been observed by others,[14] using 2-(phenylsulfonyl)-3-aryloxaziridines as the oxygen-transfer agents. Our results contrast with these in that 1 effects the oxidation rapidly and under extremely mild conditions (–50 °C, ~1 h), whereas the analogous reactions with the 2-(phenylsulfonyl)-3-aryloxaziridines require comparatively

harsh conditions (60 °C, 3 h).

Oxaziridine 1 oxidizes 2,5-dimethylfuran even more readily than it oxidizes 2,3-dimethyl-2-butene. In this case the final product is cis-3-hexene-2,5-dione. This product possibly arises from rearrangement of an intermediate epoxide, as illustrated in eq 5. The dione is not particu-
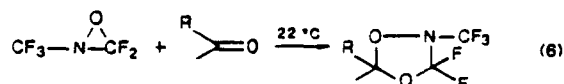
$$F_3C-\overset{\overset{O}{\|}}{N}-CF_2 \; + \; \underset{}{\text{furan}} \; \xrightarrow[-CF_3N=CF_2]{-50\,°C,\,15\,min} \; \underset{}{\text{epoxide}} \; - \; \underset{}{\text{dione}} \quad (5)$$

larly stable,[9] but we believe that our spectral data confirm it as the oxidation product. The infrared spectrum agrees with that reported in the literature[9] [strong bands for carbonyl (1685 cm^{-1}) and cis-alkene (1613 cm^{-1})], and a ^{13}C NMR spectrum reveals only signals attributable to unreacted 2,5-dimethylfuran and the dione (see Experimental Section). We attribute the red or orange color of the product mixture to condensation products of the dione.

Reaction of 1 with propene, cyclohexene, cyclopentadiene, and furan also proceeded readily to give CF_3N=CF_2 as the major fluorine-containing product. In these cases, however, the hydrocarbons were mainly converted to polymeric materials which, depending on condition and the scale of the reaction, were often a clear glasslike material. A reaction with propene carried out in $CDCl_3$ in an NMR tube while the ^{1}H and ^{19}F NMR were monitored clearly showed the rapid formation of CF_3N=CF_2, complete consumption of the propene, a small amount of propylene oxide [δ 1.32 (d), 2.4 (m), 2.8 (m)] and two major broad resonances (δ 1.1, 3.5). We conclude that these reactions are also examples of oxygen atom transfer but the oxidized products polymerize under the reaction conditions.

Finally, the reaction of 1 with CF_2=CBr_2 may indicate that oxygen atom transfer is not limited to hydrocarbon olefins. This reaction forms only a 25% yield of the cycloadduct 2f; the major products were CF_3N=CF_2 and $CFBr_2C(O)F$. These products do not arise from 2f, which has high thermal stability. Quite probably, these products arise from the formation of the intermediate epoxide, $\overline{CF_2CBr_2O}$, formed by oxygen atom transfer and subsequent rearrangement of the epoxide to $CFBr_2C(O)F$. The epoxide $\overline{CF_2CBr_2O}$ does not appear to be a known species, but our proposal is supported by the photochemical oxidation of CF_2=$CFCl$ with oxygen. This produces only a small yield of epoxide, with $CF_2ClC(O)F$ as a major product.[15]

Cycloadditions with Ketones. Oxaziridine 1 adds readily to hydrocarbon ketones (no reaction occurred with hexafluoroacetone) to afford 1,3,4-dioxazolidines (eq 6).

$$CF_3-\overset{\overset{O}{\|}}{N}-CF_2 \; + \; \underset{R}{\overset{R}{\text{>=O}}} \; \xrightarrow{22\,°C} \; R\underset{O}{\overset{O-\!\!-\!N-CF_3}{\bigvee}}F \quad (6)$$

4a, R = CH_3. **4b**, R = C_2H_5; **4c**, t-Bu; **4d**, R = CH=CH_2

These compounds are stable, colorless liquids at room temperature and were readily characterized by their mass (all show an intense M + 1 peak in their CI spectra), ^{19}F and ^{1}H NMR, and IR spectra. All exhibit a characteristic A_3B_2 pattern in the ^{19}F NMR.

These [2 + 3] cycloadditions may be explained as either an attack of the 1,3-dipolar species of 1 on the ketone, or as a nucleophilic attack of the ketone on the nitrogen of

(10) Chambers, R. D. Fluorine in Organic Chemistry; Wiley-Interscience: New York, 1973; pp 179–189. Sharkey, W. H. Fluorine Chem. Rev. 1968, 2, 1.

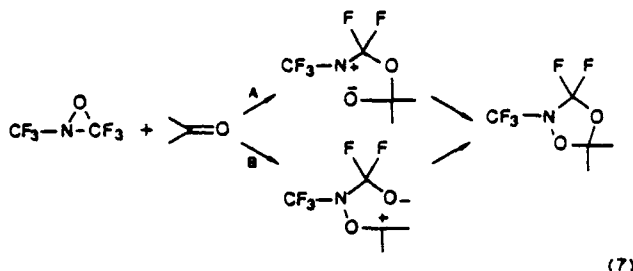(11) Banks, R. E.; Burling, E. D. J. Chem. Soc. 1965, 6077.

(12) Spectrum obtained at the Southeastern Regional Instrumentation Center, Columbia, S.C.

(13) For structurally related compounds, see: Dungan, C. H.; Van Wazer, J. R. Compilation of Reported [19]F Chemical Shifts 1951 to mid 1967; Wiley-Interscience: New York, 1970.

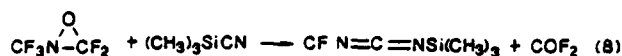(14) Davis, F. A.; Abdul-Malik, N. F.; Curad, S. B.; Harakal, M. E. Tetrahedron Lett. 1981, 22, 917.

(15) Chow, D.; Johns, M. H.; Thorne, M. P.; Wong, E. C. Can. J. Chem. 1969, 47, 2591.

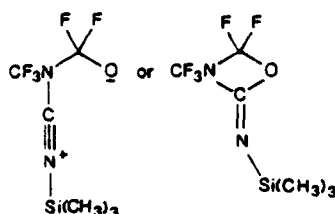1. This is shown in eq 7 for acetone.

(7)

Reaction path 7B is very plausible on the basis of the ease with which oxaziridine 1 has been shown to undergo ring opening by a variety of nucleophiles.[16] This pathway also seems more consistent with the mild reaction conditions.

Reaction with $(CH_3)_3SiCN$. One additional reaction type that is of interest in demonstrating the varied reactivity of 1 is the reaction with $(CH_3)_3SiCN$. As reported earlier, this leads to 1-(trifluoromethyl)-3-(trimethylsilyl)carbodiimide and carbonyl fluoride (eq 8). When

carried out by warming the reactants slowly from -196 to 22 °C, the reaction is quantitative. Attempts to extend this reaction to CF_3CN or CH_3CN resulted in recovery of starting materials. Since $(CH_3)_3SiCN$ has been shown to be in equilibrium with the isocyanide,[16] a reaction of *tert*-butyl isocyanide was carried out, but the latter also showed no reaction at 22 °C. Finally, in hopes of providing some insight into the mechanism of the reaction of 1, the reaction of HFPO with $(CH_3)_3SiCN$ was investigated. Surprisingly, no reaction was observed even at 150 °C.

These observations make it difficult to rationalize the observed reaction of 1 with $(CH_3)_3SiCN$. An attractive proposal involving a reaction of 1 with the isonitrile form of $(CH_3)_3SiCN$, leading to the intermediate

followed by elimination of COF_2, seems to be precluded by the failure of 1 to react with *tert*-butyl isocyanide. Similarly, a reaction involving an intermediate [2 + 3] cycloadduct of 1 to the carbon–nitrogen triple bond in either $(CH_3)_3SiCN$ or $(CH_3)_3SiNC$ suffers from a lack of precedent for such reactions.

We propose the reaction scheme in eq 9 as one consistent with the established reactivity of $(CH_3)_3SiCN$.[17] An ob-

$$CF_3N{=}C{=}NSi(CH_3)_3 + COF_2 \quad (9)$$

vious criticism of this proposal is that the intermediate might be expected to eliminate $(CH_3)_3SiF$ instead of COF_2, leading to the known compound $CF_3N(CN)COF$.[18]

Conclusion

PFAPO has now been shown to undergo a variety of reactions involving the nitrogen–oxygen bond. The three main reaction types demonstrated are (1) ring opening by nucleophiles, (2) cycloadditions with halogenated olefins and dialkyl ketones, and (3) oxygen atom transfer with electron-rich olefins. Reaction type 1 is closely analogous to that of the commercial monomer hexafluoropropene oxide (HFPO), whereas types 2 and 3 are not readily observed for HFPO. Apart from the obvious utility of PFAPO in the synthesis of novel compounds, reactions 2 (except dialkyl ketone) and 3 represent unusual reaction types for small-ring heterocycles with little or no precedent.

(16) Seckar, J.; Thayer, J. S. *Inorg. Chem.* **1976**, *15*, 1976.

(17) Groutas, W. C.; Felker, D. *Synthesis* **1980**, 861.
(18) Sekiya, A.; DesMarteau, D. D. *J. Fluorine Chem.* **1979**, *14*, 289.

The Microwave Spectrum, Harmonic Force Field, and Structure of N-Chlorodifluoromethylenimine, $CF_2=NCl$

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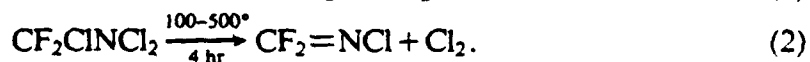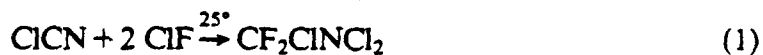*Department of Chemistry, Clemson University, Clemson, South Carolina 29631*

The microwave spectra of two isotopic species of N-chlorodifluoromethylenimine $(CF_2=NCl)$ have been measured in the frequency region 12–54 GHz. Rotational, quartic centrifugal distortion, and Cl and ^{14}N nuclear quadrupole coupling constants have been evaluated. The distortion constants have been combined with vibrational wavenumbers from the literature to calculate a harmonic force field. Effective (r_0) and ground state average (r_z) parameters have been evaluated, and have provided evidence that the structure of $CF_2=NCl$ is a hybrid of those of $CF_2=NF$ and $CCl_2=NCl$. Bonding information has been obtained from the quadrupole coupling constants.
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INTRODUCTION

The structural parameters of two perhalomethylenimines, $CF_2=NF$ and $CCl_2=NCl$, have recently been reported. Christen (*1*) made a detailed analysis of the microwave spectrum of $CF_2=NF$, which included evaluation of the ^{14}N quadrupole coupling constants. Subsequently these results were combined with infrared, Raman, and electron diffraction data along with ab initio calculations to determine a reliable structure and a harmonic force field (*2*). The infrared and Raman spectra of $CCl_2=NCl$ were reported some years ago (*3*). Recently an electron diffraction study allowed Christen and Kalcher (*4*) to determine its structure, and a more detailed investigation of its vibrational spectrum has yielded a harmonic force field (*5*).

N-chlorodifluoromethylenimine, $CF_2=NCl$, was first prepared by Young *et al.* (*6*) by the pyrolysis of CF_2ClNCl_2; the latter had been prepared from ClF and ClCN:

$$ClCN + 2\ ClF \xrightarrow{25°} CF_2ClNCl_2 \qquad (1)$$

$$CF_2ClNCl_2 \xrightarrow[4\ hr]{100-500°} CF_2=NCl + Cl_2. \qquad (2)$$

To characterize the product Young *et al.* measured its mass, ^{19}F NMR, and infrared spectra. At about the same time Hirschmann *et al.* (*7*) measured the infrared spectrum in greater detail; they observed only seven of the nine fundamentals, and had to estimate the positions of the missing two, the lowest frequency modes, from combination band

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data. Very recently O'Brien *et al.* (*8*) measured the Raman spectrum and remeasured the infrared spectrum, and were able to reevaluate the wavenumbers of the two previously unobserved fundamentals.

Arguably the most interesting structural feature of $CF_2=NF$ and $CCl_2=NCl$ is the $C=N-X$ angle, which varies from 107.9° for $\langle(C=N-F)$ in the former, to 117.1° for $\langle(C=N-Cl)$ in the latter. To obtain information on this parameter in $CF_2=NCl$ we have measured its microwave spectrum. Transitions of both the ^{35}Cl and ^{37}Cl isotopic species have been observed, and rotational, centrifugal distortion, and ^{14}N and Cl quadrupole coupling constants have been evaluated. A harmonic force field has been calculated from combined distortion and vibrational data. Partial r_0 and r_z structures have been evaluated, and information on the nature of the bonding has been obtained from the quadrupole coupling constants.

EXPERIMENTAL DETAILS

Two samples of $CF_2=NCl$ (0.1 and 0.2 g) were prepared by the method of Zheng and DesMarteau (*9*). They were stored at liquid nitrogen temperature, where they were indefinitely stable, and were brought to room temperature for sampling in the microwave study. The sample purity was checked by mass spectroscopy.

Transitions were measured in the frequency range 12–54 GHz, using a 100-kHz Stark-modulated spectrometer with a 3-m copper X-band cell. The microwave sources were a Hewlett-Packard 8400B backward wave oscillator source and a Watkins-Johnson 1291 synthesizer, equipped where necessary with Honeywell-SpaceKom frequency multipliers. In the latter stages of the work the synthesizer was controlled using a Digital Micro-PDP11 computer, which was also used for storage, signal averaging, and measurement of the spectrum. All measurements were made with the Stark cell wrapped in dry ice. Under these conditions transitions due to $CF_2=NCl$ could be observed for up to 30 min, though lines of decomposition product(s) (as yet unidentified) appeared within the first few minutes. Unfortunately the small amounts of sample precluded the use of a flow system.

OBSERVED SPECTRUM AND ASSIGNMENT

Several predictions of rotational constants were made using structural data transferred from various related molecules, such as $ClNCO$, ClN_3, CH_2NH, and OCF_2. In particular one was made using CF_2 parameters from $CF_2=NF$ and $C=N-Cl$ parameters from $CCl_2=NCl$. Cl quadrupole coupling constants were transferred from $ClNCO$ (*10, 11*). The molecule was expected to be a planar, slightly asymmetric prolate rotor with C_s symmetry, probably having both *a*- and *b*-type transitions.

The observed spectrum fitted very well (to within a few percent) to the one predicted from the combined $CF_2=NF$ and $CCl_2=NCl$ parameters, with *a*- and *b*-type transitions of comparable intensity. The initial assignments were of the $J = 7 \leftarrow 6$ and $8 \leftarrow 7$ *a*-type *R* branches, which gave preliminary values of *B* and *C*. Candidates for the *b*-type *Q* branches $6_{1,5} \leftarrow 6_{0,6}$ and $7_{1,6} \leftarrow 7_{0,7}$ were identified from their quadrupole patterns; when these were included in the fits, *A* was also evaluated. Accurate predictions of further transitions could then be made, and a bootstrap procedure was used to assign an increasing number of transitions. All transitions, for both ^{35}Cl and ^{37}Cl species,

showed Cl quadrupole structure to some extent, which along with the frequency fit, was used as a criterion for assignment. Quadrupole hyperfine structure due to ^{14}N, which was much smaller than that of Cl, was observed for a few transitions.

ANALYSIS OF THE SPECTRUM

(a) Nuclear Quadrupole Coupling

Initially the transitions showing both Cl and ^{14}N quadrupole structure were analyzed for the coupling constants. The coupling scheme given below was followed very closely:

$$\mathbf{I}_1 + \mathbf{J} \rightarrow \mathbf{F}_1; \qquad \mathbf{I}_2 + \mathbf{F}_1 \rightarrow \mathbf{F}.$$

Here $\mathbf{I}_1$ and $\mathbf{I}_2$ are the nuclear spins of chlorine and nitrogen, respectively. The splittings were well accounted for by the following first-order expression (10), which ignored effects off-diagonal in the quantum numbers J and F_1, associated with $\mathbf{J}$ and $\mathbf{F}_1$.

$$E_Q = \frac{f(I_1, J, F_1)}{J(J+1)} \left\{ [3\langle J_a^2 \rangle - J(J+1)]\chi_{aa}(1) + \left[\frac{\langle J_a^2 \rangle - W(b_p)}{b_p}\right] \cdot [\chi_{bb}(1) - \chi_{cc}(1)] \right\}$$

$$+ \frac{4(2F_1 - 1)}{(F_1 + 1)J(J+1)} f(I_2, F_1, F) \cdot f(F_1, J, I_1) \left\{ [3\langle J_a^2 \rangle - J(J+1)]\chi_{aa}(2) + \cdots \right.$$

$$\left. + \left[\frac{\langle J_a^2 \rangle - W(b_p)}{b_p}\right] \cdot [\chi_{bb}(2) - \chi_{cc}(2)] \right\}. \quad (3)$$

Here $f(\alpha, \beta, \gamma)$ is Casimir's function, $W(b_p)$ is the Wang reduced energy, and $\langle J_a^2 \rangle$ is the expectation value of the square of the angular momentum about the a-axis.

A least-squares fit of the transitions with resolved nitrogen splittings was made to the coupling constants, using Eq. (3). The resulting ^{14}N constants are in Table I; it is clear that for $CF_2 = N^{35}Cl$ all the constants are determined, but for $CF_2 = N^{37}Cl$ only $(\chi_{bb} - \chi_{cc})$ for ^{14}N could be obtained. Table II gives the measured frequencies of three transitions with resolved Cl and ^{14}N hyperfine structure; a good fit has clearly been obtained. A check was made in which the splittings were predicted by diagonalizing the full Hamiltonian rather than by using Eq. (3); effects of off-diagonal contributions were found to be insignificant.

The final Cl quadrupole constants were obtained by fitting all transitions with Cl splitting to the well-known first-order expression (12). (In this case any observed ^{14}N splittings were subtracted off.) The results are also in Table I; in this case excellent values have been obtained for all constants, for both isotopic species. Measured frequencies of some representative transitions, along with assignments and observed and calculated splittings, are given in Table III.

(b) Rotational and Centrifugal Distortion Constants

After the hyperfine structure had been subtracted off the measured transitions, using the coupling constants of Table I, the resulting unsplit line frequencies were then used to calculate the rotational constants and quartic centrifugal distortion constants. Watson's Hamiltonian in its A reduction, in the I^r representation, was used (13); no sextic constants were required to fit the data. Because some transitions were only incompletely

TABLE I

Spectroscopic Constants of CF_2NCl

		$CF_2N^{35}Cl$	$CF_2N^{37}Cl$
Rotational Constants (MHz)			
	A_0	11260.8730(48)	11260.8818(88)
	B_0	2542.2000(12)	2470.9258(15)
	C_0	2072.4246(11)	2024.8091(16)
Centrifugal Distortion Constants (kHz)			
	Δ_J	0.3584(57)	0.3667(37)
	Δ_{JK}	3.939(30)	3.813(54)
	Δ_K	8.05(12)	8.16(96)
	δ_J	0.0690(15)	0.0623(14)
	δ_K	2.546(83)	2.474(60)
Chlorine and Nitrogen Nuclear Quadrupole Coupling Constants (MHz)			
Chlorine	χ_{aa}	-70.33(41)	-54.73(67)
	χ_{bb} χ_{cc}	-26.02(15)	-20.02(18)
	χ_{cc}	48.17(22)	37.37(35)
Nitrogen	χ_{aa}	3.42(61)	7.2(11.1)
	χ_{bb} χ_{cc}	-2.822(86)	-2.67(43)
	χ_{cc}	-0.30(63)	a

[a] Not evaluated because χ_{aa} is indeterminate.

resolved, some could be only partially modulated, and some were subject to interference from transitions of the impurity molecules, the frequencies were weighted in the fits according to the confidence in their measurement accuracies; the highest accuracies were ~ ±0.03 MHz.

The resulting constants are also in Table I; it is clear that good values for all rotational and centrifugal distortion constants have been obtained. Table IV gives the frequencies of all measured transitions, along with their weights in the fits and the differences between the observed and calculated frequencies.

THE HARMONIC FORCE FIELD AND STRUCTURE

(a) The Effective Structure

The ground state principal moments of inertia and inertial defects of the two isotopic species of CF_2=NCl are given in Table V. The inertial defects are small positive numbers, which are nearly equal for the two isotopes, and therefore confirm that the molecule is planar.

The molecular structure can be described (Fig. 1) by four bond lengths (r(C=N), r(N—Cl), r(C—F_t), r(C—F_c)) and three bond angles ($\langle$(C=N—Cl), $\langle$(N=C—F_t), $\langle$(N=C—F_c)). With six rotational constants, only four of which are independent be-

TABLE II

Some Representative Transitions (MHz) of $CF_2N^{35}Cl$ Showing ^{35}Cl and ^{14}N Quadrupole Structure

Transition	F'_1 F' . F''_1 F''	Observed Frequency (MHz)	Obs Splitting (MHz)	Calc Splitting (MHz)
$5_{15}-4_{04}$	4.5 4.5 - 3.5 3.5	28653.929	-1.423	-1.428
	4.5 5.5 - 3.5 4.5	28654.255	-1.097	-1.129
	4.5 3.5 - 3.5 2.5	28654.382	-0.970	-1.010
	5.5 5.5 - 4.5 4.5	28654.874	-0.478	-0.490
	3.5 3.5 - 2.5 2.5	28654.874	-0.478	-0.480
	5.5 6.5 - 4.5 5.5	28655.240	-0.112	-0.150
	3.5 4.5 - 2.5 3.5	28655.240	-0.112	-0.120
	5.5 4.5 - 4.5 3.5	28655.240	-0.112	-0.030
	3.5 2.5 - 2.5 1.5	28655.240	-0.112	0.010
	6.5 6.5 - 5.5 5.5	28655.684	0.332	0.429
	6.5 7.5 - 5.5 6.5	28656.303	0.951	0.899
	6.5 5.5 - 5.5 4.5	28656.303	0.951	1.001
$6_{15}-6_{06}$	4.5 3.5 - 4.5 3.5	14839.067	-3.758	-3.805
	4.5 5.5 - 4.5 5.5	14839.067	-3.758	-3.681
	4.5 4.5 - 4.5 4.5	14839.691	-3.134	-3.137
	7.5 6.5 - 7.5 6.5	14840.365	-2.460	-2.470
	7.5 8.5 - 7.5 8.5	14840.365	-2.460	-2.392
	7.5 7.5 - 7.5 7.5	14840.977	-1.848	-1.810
	5.5 4.5 - 5.5 4.5	14844.701	1.876	1.778
	5.5 6.5 - 5.5 6.5	14844.701	1.876	1.873
	5.5 5.5 - 5.5 5.5	14845.293	2.468	2.388
	6.5 5.5 - 6.5 5.5	14845.976	3.151	3.094
	6.5 7.5 - 6.5 7.5	14845.976	3.151	3.177
	6.5 6.5 - 6.5 6.5	14846.471	3.646	3.710
$7_{26}-7_{17}$	5.5 4.5 - 5.5 4.5	33624.599	-3.909	-3.953
	5.5 6.5 - 5.5 6.5	33624.599	-3.909	-3.896
	5.5 5.5 - 5.5 5.5	33624.946	-3.562	-3.587
	8.5 7.5 - 8.5 7.5	33625.711	-2.797	-2.683
	8.5 9.5 - 8.5 9.5	33625.711	-2.797	-2.645
	8.5 8.5 - 8.5 8.5	33626.100	-2.408	-2.321
	6.5 5.5 - 6.5 5.5	33630.772	2.264	2.249
	6.5 7.5 - 6.5 7.5	33630.772	2.264	2.295
	6.5 6.5 - 6.5 6.5	33631.071	2.563	2.591
	7.5 6.5 - 7.5 6.5	33632.158	3.650	3.511
	7.5 8.5 - 7.5 8.5	33632.158	3.650	3.551
	7.5 7.5 - 7.5 7.5	33632.455	3.947	3.855

cause of the planarity of the molecule, unambiguous determination of a full structure is impossible. At best, determination of no more than two or three parameters of an effective (r_0) or ground state average (r_z) structure could be hoped for.

Some reasonable deductions can be made, however. There was a large variation in the rotational constants initially predicted from model structures. Those obtained using parameters transferred from $CF_2=NF$ and $CCl_2=NCl$ were excellent, by far the best, and suggest that $CF_2=NCl$ is roughly a hybrid of the two. To carry matters further some assumptions must be made; in this case we have fixed the $CF_2=N$ parameters at those of $CF_2=NF$ (2), and have varied $r(N-Cl)$ and $\langle(N=C-Cl)$. This procedure is substantially justified by the difference in $\langle(C=N-X)$ between $CF_2=NF$ and $CCl_2=NCl$.

Least-squares fits of the effective rotational constants (Table I) were made to the two variable parameters. Unfortunately simultaneous fits to both parameters were

MICROWAVE SPECTRUM OF CF$_2$=NCl

TABLE III

Observed Hyperfine Structure Due to ^{35}Cl in the Microwave Spectrum of CF$_2$NCl

Transition	F' · F"	Frequency (uncertainty) (MHz)	Obs − Calc[a] splits (MHz)
CF$_2$N^{35}Cl			
$6_{16}-5_{15}$	5.5 · 4.5	26141.859(50)	0.023
	4.5 · 3.5	26142.498(30)	0.063
	6.5 · 5.5	26142.498(30)	-0.077
	7.5 · 6.5	26143.165(30)	-0.009
$6_{34}-5_{33}$	6.5 · 5.5	27773.668(30)	-0.035
	5.5 · 4.5	27774.633(30)	-0.055
	7.5 · 6.5	27778.237(30)	0.063
	4.5 · 3.5	27779.185(30)	0.027
$8_{54}-7_{53}$	6.5 · 5.5	37008.250(30)	-0.065
	9.5 · 8.5	37007.240(30)	0.004
	7.5 · 6.5	37003.110(30)	-0.009
	8.5 · 7.5	37002.110(30)	0.070
$7_{07}-6_{16}$	5.5 · 4.5	26332.903(30)	0.063
	6.5 · 5.5	26333.245(30)	-0.023
	8.5 · 7.5	26333.587(30)	0.009
	7.5 · 6.5	26333.958(30)	-0.048
$6_{16}-5_{05}$	7.5 · 6.5	32087.123(30)	-0.022
	4.5 · 3.5	32086.600(30)	0.009
	6.5 · 5.5	32085.885(30)	-0.003
	5.5 · 4.5	32085.350(30)	0.016
$6_{15}-6_{06}$	4.5 · 4.5	14839.283(50)	0.011
	7.5 · 7.5	14840.572(30)	-0.021
	5.5 · 5.5	14844.904(30)	0.045
	6.5 · 6.5	14846.145(30)	-0.035
$12_{111}-12_{012}$	10.5 · 10.5	35596.275(30)	-0.021
	13.5 · 13.5	35599.016(30)	0.074
	11.5 · 11.5	35603.600(30)	-0.046
	12.5 · 12.5	35604.286(30)	-0.007
$7_{25}-7_{16}$	5.5 · 5.5	22773.449(50)	-0.019
	8.5 · 8.5	22773.782(50)	-0.033
	6.5 · 6.5	22775.223(50)	0.048
	7.5 · 7.5	22775.527(50)	0.004
$14_{212}-14_{113}$	12.5 · 12.5	29520.736(30)	-0.018
	15.5 · 15.5	29521.076(30)	0.020
	13.5 · 13.5	29523.601(30)	-0.057
	14.5 · 14.5	29524.015(30)	0.055

[a] Observed frequency minus the frequency calculated using the fitted spectroscopic constants.

TABLE IV

Observed Transition Frequencies (MHz), with the Hyperfine Structure Removed, of CF$_2$NCl

Transition							Frequency	Obs-Calc	Weight
CF$_2$N^{35}Cl									
5	2	4	–	6	1	5	30451.090	-0.013	1.0000
5	1	5	–	4	0	4	28655.352 [a]	0.043	1.0000
5	0	5	–	4	1	4	15878.683	-0.157	0.0000
6	2	5	–	6	1	6	31912.724	0.037	1.0000
6	2	4	–	5	2	3	28221.114	-0.019	1.0000
6	3	4	–	5	3	3	27776.362	0.033	0.0100
6	3	3	–	5	3	2	27801.612	0.007	1.0000
6	0	6	–	5	0	5	27070.136	-0.069	0.1000
6	1	5	–	6	0	6	14842.825 [a]	0.019	1.0000
6	1	6	–	5	0	5	32086.353	0.197	0.0000
6	1	6	–	5	1	5	26142.639	-0.010	0.0001
6	0	6	–	5	1	5	21126.519	-0.179	0.0000
6	2	5	–	5	2	4	27604.312	0.079	1.0000
7	2	5	–	7	1	6	22774.530	0.103	0.1000
7	2	6	–	7	1	7	33628.508 [a]	-0.017	1.0000
7	0	7	–	6	0	6	31349.563	0.009	1.0000
7	1	6	–	6	1	5	33674.168	-0.051	0.0100
7	3	5	–	6	3	4	32427.661	0.018	0.1000
7	1	7	–	6	0	6	35458.518	-0.000	0.0100
7	3	4	–	6	3	3	32484.106	-0.043	0.1000
7	0	7	–	6	1	6	26333.520	-0.084	1.0000
8	2	6	–	8	1	7	22453.480	0.040	1.0000
8	2	7	–	7	2	6	36691.501	0.051	1.0000
8	2	6	–	7	2	5	38046.288	-0.111	0.0100
8	3	5	–	7	3	4	37195.515	-0.066	1.0000
8	4	5	–	7	4	4	37043.765	-0.012	1.0000
8	1	7	–	7	1	6	38367.494	0.109	0.0000
8	1	7	–	8	0	8	34721.401	-0.076	0.0100
8	0	8	–	7	1	7	19976.286	-0.295	0.0000
8	4	4	–	7	4	3	31449.265	-0.046	0.0000
8	1	8	–	7	0	7	37046.785	-0.032	1.0000
8	5	4	–	7	5	3	38830.436	-0.005	1.0000
8	0	8	–	7	0	7	37005.110	0.040	1.0000
8	5	3	–	7	5	2	35558.237	-0.038	0.1000
9	1	9	–	8	1	8	37005.110	0.003	1.0000
9	1	8	–	8	1	7	38979.500	-0.169	0.0001
9	2	7	–	8	2	6	43004.901	-0.007	0.0100
9	0	9	–	8	2	8	43011.526	-0.141	0.0000
9	1	8	–	9	0	9	36440.291	0.058	0.0000
9	3	6	–	8	3	5	23268.840	-0.250	0.0000
9	0	9	–	8	0	8	41944.025	0.053	1.0000
9	1	8	–	8	2	7	39712.477	0.078	0.0001
10	3	7	–	10	2	8	24110.673	-0.152	0.0000
10	2	8	–	10	1	9	40096.710	0.026	0.0000
10	0	10	–	9	1	9	22866.509	0.031	1.0000
10	1	9	–	9	2	8	41291.635	-0.051	0.0001
10	1	9	–	10	0	10	30465.896	0.058	0.0000
11	2	9	–	11	1	10	27013.492	-0.242	0.0000
11	1	11	–	10	0	10	23732.212	0.026	1.0000
11	1	10	–	10	2	9	49365.369	-0.056	0.1000
12	3	9	–	12	2	10	36871.356	0.023	0.0000
12	0	12	–	11	1	11	37386.480	-0.038	1.0000
12	1	11	–	12	0	12	50594.400	-0.083	0.1000
12	1	12	–	11	0	11	35601.320 [a]	-0.021	1.0000
13	5	9	–	14	4	10	53077.076	-0.071	0.1000
13	2	12	–	13	1	13	14483.459	0.011	1.0000
13	3	10	–	13	2	11	49032.787	-0.131	0.1000
13	1	12	–	13	0	13	36124.376	-0.039	1.0000
13	2	11	–	13	1	12	40273.163	0.510	0.0000
13	2	11	–	12	3	10	27028.881	-0.052	0.1000
14	2	12	–	14	1	13	27416.442	-0.088	0.1000
14	2	12	–	13	3	11	29522.368 [a]	0.013	1.0000
14	3	11	–	14	2	12	34622.747	-0.246	0.0000
15	3	12	–	15	2	13	35076.982	-0.006	1.0000
							34352.147	-0.008	1.0000

[a] Transitions showing resolvable hyperfine structure by nitrogen.

TABLE IV—*Continued*

Transition						Frequency	Obs-Calc	Weight
15	2	13	15	1	14	32590.239[a]	0.018	1.0000
16	3	13	16	2	14	34048.222	0.023	1.0000
16	2	14	16	1	15	36209.480	0.009	0.0100
17	7	11	18	6	12	32150.286	-0.002	1.0000
17	3	14	17	2	15	34246.825	-0.115	1.0000
17	3	14	16	4	13	27392.030	-0.369	0.0000
18	3	15	18	2	16	35013.589	0.012	1.0000
18	3	15	17	4	14	34869.318	0.088	0.1000
19	2	17	19	1	18	49738.644	-0.159	0.0000
19	3	16	19	2	17	36397.027	-0.043	1.0000
20	3	17	20	2	18	38429.509	0.046	1.0000
20	4	16	20	3	17	48027.496	0.047	1.0000

CF$_2$N^{37}Cl

Transition						Frequency	Obs-Calc	Weight
5	1	5	4	0	4	28281.947	0.155	0.0000
6	2	4	6	1	5	23621.750	0.142	1.0000
6	2	5	5	2	4	26899.581	0.055	1.0000
6	2	4	5	2	3	27454.955	0.001	1.0000
6	1	6	5	0	5	31641.394[a]	-0.035	1.0000
6	0	6	5	0	5	26418.375	-0.023	0.0000
6	0	6	5	1	5	20290.538	-0.211	0.0000
7	2	5	7	1	6	23033.086	-0.129	0.0000
7	2	5	6	2	4	32200.603	0.040	1.0000
7	3	5	6	3	4	31583.592	-0.001	1.0000
7	3	4	6	3	3	31631.352	-0.068	1.0000
7	0	7	6	0	6	30609.268	0.028	0.0001
7	1	7	6	1	6	29714.189	-0.024	0.0001
7	1	6	6	1	5	32788.940	-0.016	0.0001
7	0	7	6	1	6	25386.166	-0.043	0.0000
7	2	6	6	2	5	31340.966	-0.080	1.0000
8	2	7	8	1	8	35326.000	-0.145	1.0000
8	2	6	8	1	7	22657.707	-0.033	1.0000
8	0	8	7	0	7	34732.721	0.033	0.0001
8	1	8	7	1	7	33895.487	0.170	0.0000
8	1	8	7	0	7	38223.368	0.047	1.0000
8	0	8	7	1	7	30404.644	-0.040	0.0000
8	1	7	7	1	6	37369.099	0.024	0.0100
8	2	6	7	2	5	36993.607	0.007	0.0100
9	1	8	9	0	9	22473.297[a]	0.072	1.0000
9	0	9	8	1	8	35311.351	0.035	0.0001
10	3	7	10	2	8	40754.324	0.041	0.1000
10	0	10	9	1	9	40088.319	0.199	0.0000
10	2	8	10	1	9	22854.693	0.012	1.0000
10	1	9	9	2	8	28665.904	-0.023	0.1000
11	1	11	10	0	10	48439.057	-0.486	0.0000
11	1	10	10	2	9	34899.338	-0.082	0.1000
12	3	9	12	2	10	38120.798	-0.054	1.0000
12	1	12	11	0	11	52032.491	0.025	0.0000
12	0	12	11	1	11	49254.618	0.002	1.0000
12	2	11	11	2	10	53220.156	-0.094	0.0000
13	3	11	13	2	12	50195.851	0.057	1.0000
13	3	10	13	2	11	36839.012	-0.088	0.0000
13	0	13	12	1	12	53669.541	0.065	1.0000
13	1	12	13	0	13	38691.460	-0.128	0.1000
13	2	11	13	1	12	26400.138	0.026	1.0000
13	2	11	12	3	10	24682.904	0.010	0.1000
14	3	11	14	2	12	35718.300	-0.017	1.0000
14	1	13	13	2	12	53231.433	-0.094	0.1000
14	2	12	14	1	13	28612.738	-0.017	1.0000
14	2	12	13	3	11	31648.477	-0.011	0.1000
15	3	12	15	2	13	34862.596	0.130	0.0000
15	2	13	15	1	14	31372.363	-0.018	1.0000
15	2	13	14	3	12	38755.237	-0.449	0.0000
15	1	14	15	0	15	48070.442[a]	0.017	1.0000
16	3	13	16	2	14	34367.037	-0.012	1.0000

TABLE IV—*Continued*

Transition	Frequency	Obs-Calc	Weight
$16_{2,14} - 16_{1,15}$	34668.546[a]	0.013	1.0000
$16_{1,15} - 16_{0,16}$	52807.612	-0.150	0.0000
$17_{3,14} - 16_{4,13}$	23695.250	0.031	0.0000
$17_{3,14} - 17_{2,15}$	34314.413	-0.040	1.0000
$17_{2,15} - 16_{3,14}$	53188.238	-0.031	1.0000
$17_{2,15} - 17_{1,16}$	38465.531	-0.137	0.0000
$18_{3,15} - 17_{4,14}$	30821.306	0.009	1.0000
$18_{3,15} - 18_{2,16}$	34772.247	0.028	1.0000
$19_{3,16} - 18_{4,15}$	38251.635	-0.037	0.0000
$19_{2,17} - 19_{1,18}$	47301.586	0.560	0.0000
$20_{4,16} - 20_{3,17}$	49341.578	0.010	1.0000
$20_{3,17} - 20_{2,18}$	37415.402	-0.098	0.0000

meaningless because they were perfectly correlated; this arose because the Cl atom is very near the a-inertial axis (Fig. 1). Instead we have fixed $r(N-Cl)$ at several assumed values, and fit solely to $\langle(C=N-Cl)$. The results with various values of $r(N-Cl)$, including those found in $CCl_2=NCl$, ClNCO, and ClN_3 (*14*), are in Table VI.

Even this procedure has produced values with large uncertainties. It is interesting, however, that when $r(N-Cl)$ is assumed to be the same as in $CCl_2=NCl$ the same

TABLE V

Principal Moments of Inertia[a] and Inertial Defects ($\mu\text{Å}^2$) of the Effective and Average Structures of CF_2NCl

Parameter	$CF_2N^{35}Cl$	$CF_2N^{37}Cl$
Effective Structure		
I_a	44.879206(19)	44.879171(70)
I_b	198.79594(10)	204.53024(13)
I_c	243.85883(13)	249.59343(20)
Δ_0	0.18368(25)	0.18398(40)
Average Structure		
I_a	44.9518984	44.9513035
I_b	198.987165	204.724696
I_c	243.939110	249.675675
Δ_z	0.000046	-0.000325
Δ_0(calc)[b]	0.183634	0.184305

[a] Calculated using the rotational constants of Table 1 using the conversion factor 505379.045 $\mu\text{Å}^2$.

[b] From the harmonic force field refinement.
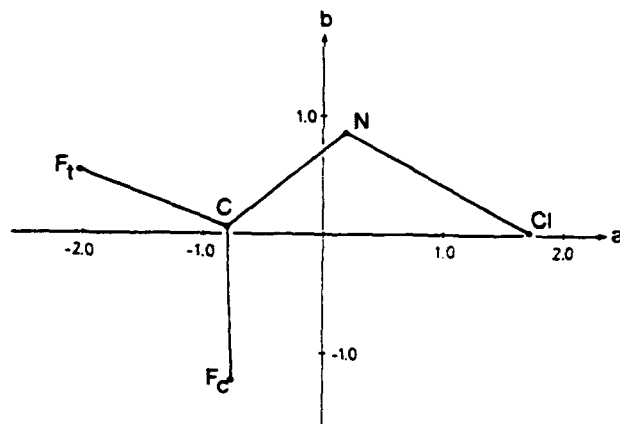
FIG. 1. The coordinates of $CF_2 = {}^{14}N^{35}Cl$ in its principal inertial axis system. The structure is the r_z structure with $r(N-Cl) = 1.745$ Å.

angle is also obtained. The uncertainty of the fit is reduced enormously when $r(N-Cl)$ is the same as in ClN_3; in this case the value of the angle is midway between that of CF_2=NF and CCl_2=NCl.

(b) The Harmonic Force Field

Because of the poor effective parameters described above, an attempt has been made to evaluate ground state average (r_z) parameters. For this purpose it was necessary to calculate harmonic contributions to the vibration–rotation α constants, which in turn required knowledge of the harmonic force field. Although strictly speaking a complete force field was required, in practice it was sufficient to have good values for the more important force constants. In this work we have evaluated an approximate force field by a least-squares fit to the combined vibrational wavenumbers (7, 8) and centrifugal distortion constants. The structural parameters used, which are those of the final r_z structure, are given in Table VII. This table also gives the chosen nonredundant symmetry coordinates, which transform as $7A' + 2A''$ in C_s. Because there can be a problem in defining the out-of-plane coordinates their B-matrix elements are also given in this table (in rad Å^{-1}).

The wavenumbers used were those of O'Brien et al. (8), which, except for the values for ν_7 and ν_9, were identical to those of Hirschmann et al. (7). In the least-squares fit a somewhat arbitrary weighting scheme was devised in which all wavenumbers were assigned uncertainties of 1%, except for ν_7 and ν_9 which, because they were overlapped, were given uncertainties of 5 and 10%, respectively. The distortion constants were given uncertainties of 2%, except for δ_K for which it was 4%. The weights were proportional to (uncertainty)$^{-2}$.

Preliminary estimates of the force constants were made by transferring values from CF_2=NF (2) and CCl_2=NCl (5). For CF_2=NF, 21 of 31 possible force constants had been obtained from combined vibrational data and ab initio calculations, and were therefore taken to be legitimate. For CCl_2=NCl the constants had been obtained from limited vibrational data, and only values which were subsequently refined were transferred.

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TABLE VI

Derived Structural Parameters of CF_2NCl: Variation of Bond Angle, $<(C=N-Cl)$, with Change in Bond Length, $r(N-Cl)$

Values of Structural Parameters Kept Fixed in all Refinements [a]

$r(C=N)$	1.273Å	$<(N-C-F_c)$	127.2°
$r(C-F_c)$	1.300Å	$<(N-C-F_t)$	119.8°
$r(C-F_t)$	1.300Å		

Bond Length from	$r(N-Cl)$ [b]	Effective (r_0)		Average (r_z)	
		$<(C=N-Cl)$	s.d. [c]	$<(C=N-Cl)$	s.d.
CCl_2NCl [d]	1.683Å	115.7±19.4°	6.7	115.8±12.4°	4.3
$ClNCO$ [e]	1.705Å	114.3±15.1°	5.3	114.4±8.2°	2.9
ClN_3 [f]	1.745Å	111.9±7.2°	2.6	112.0±0.4°	0.14
–	1.788Å	109.5±3.1°	1.2	109.6±8.1°	3.1

[a] From reference (5). Definitions of F_c and F_t are in Fig 1.
[b] Kept fixed in the refinement.
[c] Standard Deviation of refinement (MHz).
[d] Reference (7).
[e] Reference (9).
[f] Reference (11).

Deciding on how many, and which, force constants to release in the fits was a complex process, and many fits were attempted. It was found early on that releasing only the diagonal constants produced nonconvergence and that some off-diagonal constants must be released; the Jacobians were used to decide which to choose. It was ultimately necessary to constrain certain diagonal constants, notably f_{33} and f_{44}, the C—F stretching constants. The constant f_{67} was also constrained because when it was released it was nearly perfectly correlated with f_{77}. The maximum number of variable constants turned out to be 9, a reasonable value given that there were 17 pieces of independent data (8 independent distortion constants and 9 wavenumbers).

The final force field is given in Table VIII. It was chosen because all its constants are well determined, it had no large correlations, and it predicted the observed wavenumbers and distortion constants pleasingly well, as can be seen in Table IX. Its reliability was further confirmed by an excellent prediction of the inertial defect, shown in Table V.

(c) The Average Structure

The harmonic force field of Table VIII was used to calculate the harmonic parts of the α constants, and hence the ground state average rotational constants of the two isotopic species. The resulting average moments of inertia are in Table V. The average inertial defects Δ_z are essentially zero, confirming further that the molecule is planar.

TABLE VII

Structural Parameter, Internal Coordinates, and B-Matrix Elements
Used in the Normal Coordinate Analysis of CF_2NCl

Internal Coordinates and Geometry[a]

A' block
r_1 = $r(C=N)$ = 1.273Å
r_2 = $r(N\text{-}Cl)$ = 1.745Å[b]
r_3 = $r(C\text{-}F_c)$ = 1.300Å
r_4 = $r(C\text{-}F_t)$ = 1.300Å
a_1 = <C-N-Cl = 112.0°[b]
β_1 = <N-C-F_c = 127.2°
β_2 = <N-C-F_t = 119.8°

A" block
γ = CF_2 out-of-plane bend (oop)
τ = torsion angle

Symmetry Coordinates

A' block
S_1 = Δr_1
S_2 = Δr_2
S_3 = Δr_3
S_4 = Δr_4
S_5 = Δa_1
S_6 = $\Delta \beta_1$
S_7 = $\Delta \beta_2$

A" block
S_8 = $\Delta \gamma$
S_9 = $\Delta \tau$

B Matrix Elements of the Out-of-Plane Coordinates[c]

	C	N	Cl	F_c	F_t
S_8	2.0500	-0.7399	0.0000	-0.6832	-0.6269
S_9	-0.7289	1.6166	-0.9441	0.6832	-0.6269

---

[a] From reference (5) unless determined in this work. Definitions of F_c and F_t are in Fig 1.
[b] Determined in this work as an average structure.
[c] All values given are out-of-plane components, as all other components are zero.

The procedure for determining the r_z parameters was the same as that described above for the r_0 parameters, except that the average moments of inertia were used. The assumed Cl—N lengths were the same as before. The results are in Table VI. Somewhat surprisingly the angles are essentially the same as in the effective structure. The uncertainties, however, are much less (because the average inertial defect is negligible) but are still somewhat larger than ideal. The angle obtained with $r(N—Cl)$ = 1.745 Å is sufficiently certain, however, that it can be taken as the most reasonable, especially as the uncertainty increases as $r(N—Cl)$ is increased further. It is noticeable that $\langle(C=N—Cl)$ = 112.0°, midway between $\langle(C=N—X)$ of CF_2=NF (107.9°) and of CCl_2=NCl (117.1°). The N—Cl length is much greater than that in CCl_2=NCl.

TABLE VIII

The Harmonic Force Field[a] of CF_2NCl

Parameter	Value	Parameter	Value
Species A'			
f_{11}	$8.69(36)^b$	f_{34}	0.773^c
f_{12}	0.0	f_{35}	0.0
f_{13}	0.0	f_{36}	-0.01^c
f_{14}	0.0	f_{37}	-0.765^c
f_{15}	0.0	f_{44}	7.49^c
f_{16}	0.367^c	f_{45}	0.0
f_{17}	0.367^c	f_{46}	-0.765^c
f_{22}	4.21(33)	f_{47}	-0.01^c
f_{23}	0.0	f_{55}	1.441(37)
f_{24}	0.0	f_{56}	0.377(42)
f_{25}	1.22(15)	f_{57}	0.0
f_{26}	0.0	f_{66}	2.560(100)
f_{27}	0.0	f_{67}	1.374^c
f_{33}	7.53^c	f_{77}	2.513(60)
Species A"			
f_{88}	0.551(23)	f_{99}	0.207(66)
f_{89}	0.007^c		

[a] Units are mdyn/Å for stretching constants, mdyn Å/rad² for bending constants, and mdyn/rad for stretch-bend interactions.

[b] Numbers in parentheses are one standard deviation in units of the last significant figures. Force constants without numbers in parentheses were kept constrained in the refinement.

[c] Values transferred from harmonic force field of CF_2NF (5).

DISCUSSION

Although we do not have enough isotopic data to reach definite conclusions, it seems fairly clear that the structure of $CF_2=NCl$ is a hybrid of those of $CF_2=NF$ and $CCl_2=NCl$. This conclusion depends substantially on the validity of transferring bond lengths and angles from $CF_2=NF$ to $CF_2=NCl$. We have had little choice in the matter, however, and it is encouraging that the CN stretching frequencies are the same in the two molecules. The C—Cl bond would appear to be much longer in $CF_2=NCl$ than in $CCl_2=NCl$, and much nearer the sum of the single bond radii (1.73 Å) (15).

The force field is probably also the best available from the experimental data alone. It is interesting that the CN stretching constant is lower than in $CF_2=NF$. This may be the result of the constraints chosen. However, the uncertainty of our value is large, and the two constants agree within one standard deviation.

The quadrupole coupling constants also contain structural information. Since the molecule is planar the ratio of the coupling constants $\chi_{cc}(^{35}Cl)/\chi_{cc}(^{37}Cl)$ should be the ratio of the quadrupole moments of the nuclei (1.2688). The value obtained is 1.289 ± 0.024, which is in fair agreement.

TABLE IX

Observed and Calculated Wavenumbers and Centrifugal Distortion Constants of CF$_2$NCl

	CF$_2$N^{35}Cl			CF$_2$N^{37}Cl		
	obs[a]	calc[b]	obs-calc	obs[a]	calc[b]	obs-calc
Wavenumbers (cm^{-1})						
ν_1	1728.0	1732.0	-4.0	—	1731.9	
ν_2	1322.0	1359.0	-37.0	—	1359.0	
ν_3	981.0	977.5	3.5	—	976.3	
ν_4	771.0	769.7	1.2	—	767.0	
ν_5	598.0	594.2	3.8	—	594.0	
ν_6	465.0	467.5	-2.5	—	463.1	
ν_7	228.0	230.5	-2.5	—	228.4	
ν_8	658.0	658.0	0.0	—	658.0	
ν_9	234.0	234.0	0.0	—	233.2	
Centrifugal Distortion Constants (kHz)						
Δ_J	0.358	0.376	-0.017	0.367	0.360	0.007
Δ_{JK}	3.939	3.952	0.013	3.813	3.820	0.007
Δ_K	8.05	8.094	0.044	8.16	8.242	-0.082
δ_J	0.069	0.067	0.002	0.062	0.063	-0.001
δ_K	2.546	2.545	-0.001	2.474	2.457	-0.017

[a] Observed wavenumbers are from reference (3). Observed distortion constants are from this work.

[b] Calculated values were obtained from the harmonic force field given in Table VIII.

The principal values of the Cl quadrupole coupling tensor were determined for CF$_2$=N^{35}Cl. In the absence of a value for the off-diagonal constant χ_{ab}, it was necessary to assume that the ClN bond is a principal axis (the z-axis). The structure was taken to be the r_z structure with r(N—Cl) = 1.745 Å. The principal values obtained were χ_{zz} = -111.72 MHz, χ_{yy} = χ_{cc} = 48.18 MHz, χ_{xx} = 63.54 MHz.

The value of χ_{zz} is very near that of the Cl atom. Since chlorine and nitrogen have essentially the same electronegativity, such a value is to be expected if the ClN bond is essentially covalent (16). Since, in fact $|\chi_{zz}|$ = 111.72 MHz is slightly larger than $|\chi_{Cl\ atom}|$ = 109.7 MHz, any ionic character will be due to forms containing Cl$^+$ (not Cl$^-$). The difference χ_{xx}-χ_{yy} gives a measure of the double bond character of the bond (17, 18). This value is ~9%. With this in mind, and ignoring any effects of hybridization or screening at Cl, the ionic character is found to be ~7% and the covalent single bond character ~84% (16, 19).

The ^{14}N coupling constants also contain structural information. Since the b-inertial axis is very nearly parallel to the bisector of the ClNC angle, we have taken it to be a principal axis of the ^{14}N quadrupole tensor. An attempt was made to relate orbital

populations to the coupling constants using Townes–Dailey theory ($16, 19$). The ^{14}N atomic constant eQq_{210} was taken to be -10 MHz.

The calculations were done assuming sp^2 hybridization at N. The basis $2p$ orbitals were taken to be ϕ_{pa}, ϕ_{pb}, ϕ_{pc}, directed parallel to the corresponding inertial axes, with populations n_a, n_b, n_c, respectively. The "lone pair" hybrid orbital (ψ_{LP}, population n_{LP}) is parallel to the b-axis; the remaining hybrid orbitals are directed toward Cl (ψ_{NCl}, population n_{NCl}) and C (ψ_{NC}, population n_{NC}). The orbital perpendicular to the molecular plane is the pure $2p$ orbital ϕ_{pc}. The actual hybrid orbitals used were those suggested by Gordy and Cook, taking account of the fact that $\langle(Cl-N{=}C) = 112°$, rather than $120°$ (Ref. (19), Eqs. (14.115) and (14.130)). These gave the following relations between basis and hybrid orbital populations:

$$n_a = \frac{1}{2}(n_{NC} + n_{NCl})$$

$$n_b = 0.2275(n_{NC} + n_{NCl}) + 0.5446 n_{LP}$$

$$n_c = n_c. \tag{4}$$

Since four hybrid orbital populations were to be related to two experimental coupling constants, two populations were assumed. Following Ref. (11), these were taken to be $n_{NCl} = 1.07$, from the ionic character of Cl, and $n_{NC} = 1.1$, from the electronegativity difference of C and N. Two calculations were then performed: (i) With $n_{LP} = 2$ and $n_c = 1$, χ_{bb} was found to be -5.4 MHz, in poor agreement with experiment. (ii) Starting from the observed coupling constants, n_{LP} was found to be 1.88 and n_c was 1.33; these are reasonable figures, and suggest in particular considerable out-of-plane π-donation to N.

The results of the ^{14}N calculations are summarized in Table X. This table also contains for comparison purposes the results of an ab initio calculation, using a Gauss-

TABLE X

Observed and Calculated ^{14}N Quadrupole Coupling Constants (MHz) in CF_2NCl

Parameter	Experimental	Calculated	
		Ab Initio	sp^2 hybrid orbitals
χ_{aa}	3.42	4.66	2.08
χ_{cc}	-0.30	-1.39	3.32
χ_{bb}	-3.12	-3.27	-5.40
n_a	1.082[a]	0.856	1.082
n_c	1.330[a]	1.260	1.000
n_b	1.519[a]	1.385	1.582

[a] Calculated using sp^2 hybrid orbital wavefunctions and experimentally determined quadrupole coupling constants, as described in the text.

ian 70 computer program with an STO-3G basis set. The structure was the r_z structure with $r(\mathrm{N-Cl}) = 1.745$ Å. The agreement of the calculated ^{14}N orbital populations with those obtained by method (ii) above, and of the calculated ^{14}N coupling constants with the experimental values, is quite good. The same calculation also gave $3p$ orbital populations at Cl; it is interesting that the ^{35}Cl coupling constants derived from them are $\chi_{aa} = -61.4$ MHz, $\chi_{bb} = 15.4$ MHz, and $\chi_{cc} = 46.1$ MHz, also in good agreement with experiment.

ACKNOWLEDGMENTS

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Gasphasen-Reaktionen, 59 [1. 2]
Die Pyrolysen von Trifluormethylazid und Hexafluorazomethan

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Trifluoromethyl azide decomposes in a low-pressure flow system at rather high temperatures by splitting off N_2. The nature of the resulting products depends largely on the wall material of the pyrolysis tube: using molybdenum above 1120 K. FCN is observed exclusively. Neither $F_2C=NF$ nor $F_3C-N=N-CF_3$ can be detected as intermediates by comparing their PE spectra with those continuously recorded while increasing the temperature. $F_3C-N=N-CF_3$ fragments already at 870 K to give N_2 and F_3C-CF_3. The PE spectra of F_3CN_3 and $F_2C=NF$ are assigned based on MNDO calculations.

Die thermische Zersetzung kovalenter Azide ist wegen der häufig nachweisbaren reaktiven Zwischenprodukte und den hieraus erhältlichen Informationen über den Reaktionsablauf von Interesse [1−7]. Azid-Pyrolysen können in der Gasphase mit PE-spektroskopischer Echtzeit-Analytik [8] gefahrlos studiert werden: Die Ausgangssubstanzen sind in der Regel nur als Flüssigkeiten explosiv. und es genügen bei einem Druck von etwa 10^{-2} mbar Millimol-Mengen. um innerhalb weniger Stunden in einem aufheizbaren Strömungsrohr zwischen 300 K und 1200 K fortlaufend die Ionisationsmuster der Gase zu registrieren. Aus den Änderungen dieser „Reaktions-Fingerabdrücke" läßt sich die N_2-Abspaltungstemperatur ablesen. und es können die Hauptprodukte der Azid-Zersetzung durch Vergleich mit ihren meist literaturbekannten PE-Spektren identifiziert werden [8].

Die Pyrolyse von Alkylaziden führt − bei Abwesenheit von Nachbargruppen-Effekten wie im Falle von Vinylazid [5] − unter 1.2-Wanderung von R=H oder CH_3 zu Alkaniminen [1−7]. welche bei tiefen Temperaturen in Substanz isoliert werden können [2. 3]:

$$\underset{X}{\overset{R}{}} \underset{Y}{\overset{}{}} C-N_3 \xrightarrow[-N_2]{\Delta T} \underset{X}{\overset{Y}{}} C=N \overset{R}{} \quad (1)$$
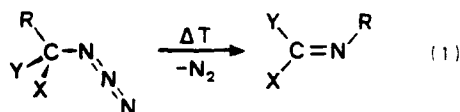
Alkylazide mit Akzeptor-Substituenten X und Y sollten daher einen einfachen Zugang zu C-Akzeptor-substituierten Iminen eröffnen. Das zunächst untersuchte Difluormethylazid F_2HC-N_3 liefert jedoch ein unerwartetes Ergebnis [7]: Seine Pyrolyse beginnt bei 720 K und verläuft oberhalb 940 K vollständig nach:

$$F_2HC-N_3 \xrightarrow{940\,K} N_2 + HF + FCN \quad (2)$$
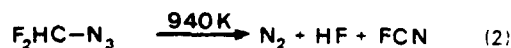
Die Zersetzungstemperatur liegt 100 K über der des unsubstituierten Methylazids [4]. aus dem unter N_2-Abspaltung und 1.2-H-Wanderung zunächst $H_2C=NH$ und erst bei weiterer Temperaturerhöhung unter H_2-Eliminierung das stabile Endprodukt HCN entsteht [4]. Im Gegensatz hierzu werden bei der Umsetzung (2) charakteristische PES-Banden für das Imin $F_2C=NH$ nicht beobachtet. obwohl MNDO-Energiehyperflächenberechnungen [7] für die HF-Abspaltung zu FCN eine relativ hohe Barriere von etwa 120 kJ/mol voraussagen. Als Erklärung wird daher „chemische Aktivierung" vorgeschlagen [9]: Zu der bei 940 K erheblichen Aktivie-

rungsenthalpie für die F_3CN_3-Zersetzung ist die Reaktionsenthalpie der stark exothermen N_2-Abspaltung zu addieren. und die entstehenden Moleküle $F_2C=NH$ enthalten somit einen erheblichen „Energieüberschuß". Dieser kann unter näherungsweise unimolekularen Zersetzungsbedingungen nicht mehr effektiv „dissipiert" werden. und die Zwischenverbindung $F_2C=NH$ sollte daher unter Ausstoß des thermodynamisch günstigen Abgangsmoleküls HF „zerplatzen" [2. 3. 7].

Für das perfluorierte Homologe Trifluormethylazid F_3C-N_3 ist keine analoge Eliminierung zu erwarten. da F_2 eine denkbar schlechte Abgangsgruppe darstellt. Bei seiner thermischen Zersetzung

$$F_3C-N_3 \xrightarrow[-N_2]{T_1} \left(F_2C=NF\ ?\right) \xrightarrow[-F_2]{T_2} FCN \quad (3)$$
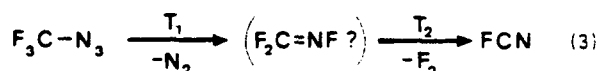
sollte daher das in Substanz isolierbare Perfluormethanimin [10] gegebenenfalls nachweisbar sein.

A. Die PE-Spektren von F_3C-N_3 und $F_2C=NF$

Für die PES-Analytik von Thermolyse-Gasgemischen [8] ist es von Vorteil. die Ionisationsmuster der unzersetzten Ausgangsverbindung sowie zu erwartender Zersetzungsprodukte vorab einzeln aufzunehmen. Trifluormethylazid F_3C-N_3 ist durch Reaktion von F_3C-NO mit N_2H_4 [11] und anschließender Oxidation durch Cl_2. und Perfluormethanimin $F_2C=NF$ durch Umsetzung von ClCN mit F_2 und ClF [10] in Substanz darstellbar (vgl. Exp. Teil). Die PE-Spek-

tren von N_2 [12]. F_2 [13] und CN [14] sind literaturbekannt.

Das PE-Spektrum von F_3C-N_3 (Abb. 1) zeigt bei 11.45 eV und 12.87 eV 2 Einzelbanden: zwischen
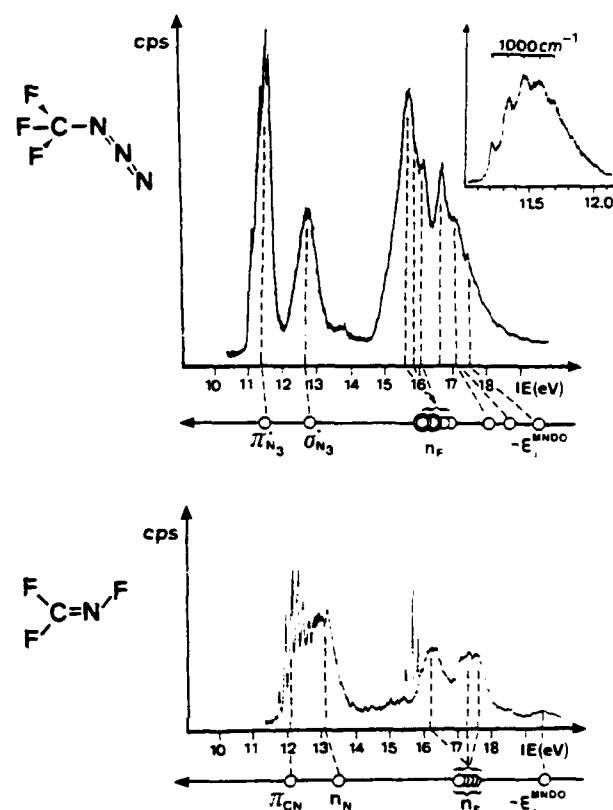
Abb. 1. He(I)-PE-Spektren von Trifluormethylazid und Perfluormethanimin mit Zuordnung anhand von MNDO-Rechnungen (vgl. Text).

Tab. I. Vertikale Ionisierungsenergien IE_n. MNDO-Eigenwerte $-\varepsilon_j^{MNDO}$ und Symmetriezuordnung der $M^{\cdot\ominus}$-Zustände für F_3C-N_3. $F_2C=NF$ und FCN (vgl. Text).

F_3C-N_3 IE_n (eV)	$-\varepsilon_j^{MNDO}$ (eV)	Typ (C_s)	$F_2C=NF$ IE_n (eV)	$-\varepsilon_j^{MNDO}$ (eV)	Typ (C_s)	FCN IE_n (eV)	$-\varepsilon_j^{MNDO}$ (eV)	Typ $(C_{\infty v})$
11.45	11.53	a'' $\pi_{N_3}^*$	12.10	12.08	a'' $\pi_{C=N}$	13.60	13.29	$^2\Pi$
12.87	12.97	a' $\sigma_{N_3}^*$	13.05	13.53	a' n_N	14.47	15.72	$^2\Sigma^-$
	16.19	a'' n_F^π	16.4	17.11	a'	19.3	18.68	$^2\Pi$
15.85	16.20	a' n_F^σ		17.26	a''			
16.15	16.42	a'' n_F^π	17.4	17.35	a'			
16.4	16.55	a' n_F^σ	17.7	17.52	a'			
	16.70	a'' n_F^π		17.63	a''			
	16.96	a'' n_F^π	19.7	19.76	a''			
16.98	18.08	a' σ_{N_3}		20.55	a'			
17.4	18.85	a'' π_{N_3}						
	19.76	a'						
17.85	20.25	a''						
	20.28	a'						

15 eV und 19 eV überlappen nach Koopmans-Korrelation. $IE_n = -\varepsilon_j^{MNDO}$, mit MNDO-Eigenwerten (Tab. I) mindestens 11 weitere Ionisierungen. Die detaillierte Zuordnung weiterer Banden, insbesondere im n_F-Bereich zwischen 15.5 und 18 eV, ist wegen der hohen Zustandsdichte in dieser Region schwierig. Das PE-Spektrum von F_3C-N_3 ähnelt erwartungsgemäß dem von F_2HC-N_3 [7]: die Zuordnung (Abb. 1 und Tab. I) läßt sich zumindest für die charakteristischen Ionisierungen in die drei niedrigsten Radikalkation-Zustände mit überwiegenden Anteilen der N_3-Gruppe $\tilde{X}(\pi_{N_3}^*)$, $\tilde{A}(\sigma_{N_3}^*)$ und σ_{N_3} (4) durch Zustandsvergleich mit anderen kovalenten Aziden stützen:

(4)

R = CF$_3$ CF$_2$H[7]   H[14]   CH$_3$[4]   C(CH$_3$)$_3$[2]
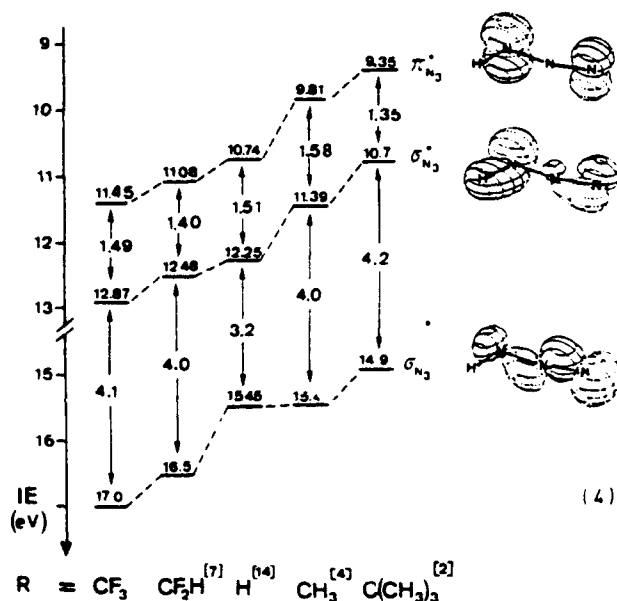
Die erste Ionisierungsenergie $(\pi_{N_3}^*)$ von F_3C-N_3 ist im Vergleich zu Methylazid [4] um 1.64 eV und zu F_2HC-N_3 [7] um 0.37 eV erhöht, die zweite Ionisierung $(\sigma_{N_3}^*)$ liegt 1.5 eV höher als die von Methylazid und 0.4 eV höher als die von F_2HC-N_3. Relativ zur Stammverbindung HN_3 [15] treten die Donor-Effekte von Alkylgruppen und die Akzeptorwirkung von Fluormethyl-Substituenten deutlich hervor (4). Auch in diesem Falle erhöht der literaturbekannte Perfluoralkyl-Effekt [13] die Ionisierungsenergien von π- und σ-Zuständen um vergleichbare Beträge. Hingewiesen sei abschließend auf die in der ersten Ionisierungsbande von F_3C-N_3 erkennbare Schwingungsfeinstruktur mit $\nu^\oplus \sim 1000$ cm^{-1} (Abb. 1: Insert), deren $O \rightarrow O$-Übergang im Gegensatz zu

H_3C-N_3 [4] nur eine geringe Intensität aufweist. Die hierdurch nahegelegte Strukturänderung bei Ionisation in den Grundzustand des Radikalkations $F_3C-N_3^\ominus$ läßt sich durch closed und open shell MNDO-Rechnungen unter Geometrieoptimierung reproduzieren [2]:
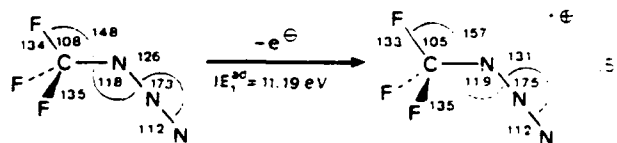
Augenfällig ist der verlängert vorausgesagte C-N-Bindungsabstand.

Für das 30-Valenzelektronen-Molekül $F_2C=NF$ werden im He(I)-Meßbereich nach einer nützlichen Faustregel [16] 10 Ionisierungen erwartet. Von diesen lassen sich 9 im PE-Spektrum bis 20 eV (Abb. 1) durch Koopmans-Korrelation mit MNDO-Eigenwerten (Tab. I) auffinden: erneut behindert die hohe Zustandsdichte zwischen 16-18 eV eine detaillierte Zuordnung in diesem Bereich. Die beiden Ionisierungen niedriger Energie führen in die für Imine charakteristischen Radikalkation-Zustände $\tilde{X}(\pi_{CN})$ und $\tilde{A}(n_N)$: relativ zum Grundkörper $H_2C=NH$ [2, 4] erfolgt somit Sequenzumkehr:

(6)
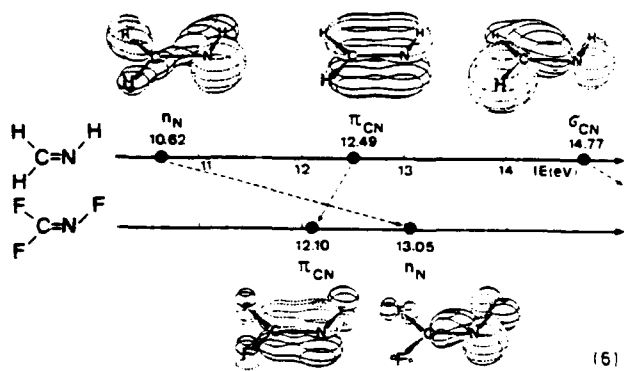
Erwartungsgemäß [17] erhöht "Perfluor-Substitution" des planaren Methanimins infolge der größeren effektiven Kernladung von F alle σ-Ionisierungsenergien, während durch "$n_F \rightarrow \pi$-Rückbindung" die Lage der π_{CN}-Bande relativ zu Methanimin weitgehend unverändert bleibt. Die Differenz der beiden niedrigsten MNDO-Eigenwerte beträgt 1.45 eV (Tab. I): nach ΔSCF(MNDO)-Berechnungen sollte

die n_N-Bande bei 13.01 eV liegen und daher mit der π_{CN}-Bande überlappen. Für den $F_2C=NF^{\ominus}$-Grundzustand $\tilde{X}(^2A'')$ wird ein längerer Bindungsabstand $d_{C=N}$ berechnet:

$$\text{(7)}$$

$$\text{M: }\tilde{X}(A') \qquad\qquad \text{M}^{\oplus}\text{: }\tilde{X}(A'')$$
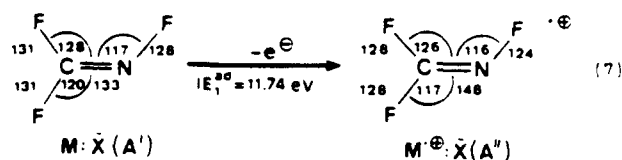
Dieser Befund läßt für die π_{CN}-Bande eine längere Progression der $C=N$-Valenzschwingung ($\nu_{MNDO} = 980\ cm^{-1}$) mit Maximum bei hohem $\nu^{\ominus}$ erwarten (vgl. Abb. 1). Für Methanimin wird bei Ionisation in den π_{CN}-Radikalkationzustand eine geringere Verlängerung des CN-Abstandes von 128 pm auf 136 pm berechnet [2]; damit übereinstimmend ist der O→O-Übergang der zweiten Bande der intensivste. Ähnliche Unterschiede werden bei den Molekülpaaren $H_2C=CH_2 \Leftrightarrow F_2C=CF_2$, $H_2C=O \Leftrightarrow F_2C=O$ und $H_2O \Leftrightarrow F_2O$ [17] gefunden. MNDO-Rechnungen sagen für $F_2C=NF^{\ominus}$ zugleich eine hohe N-Inversionsbarriere von etwa 140 kJ/mol voraus, die relativ zu der des Neutralmoleküls $F_2C=NF$ ([2]: 195 kJ/mol) nur um 50 bis 60 kJ/mol verringert sein sollte. Im Gegensatz hierzu werden für Imin-Radikalkationen wie $H_2C=NH^{\ominus}$, bei denen die Ionisierung aus dem n_N-Elektronenpaar erfolgt (6), stark aufgeweitete Bindungswinkel ∢CNR und erheblich erniedrigte Inversionsbarrieren berechnet ([2]: z.B. für $H_2C=NH$ ein Winkel ∢CNH 156° und eine Barriere von nur 3 kJ/mol).

Das literaturbekannte PE-Spektrum von FCN [14] (Abb. 2) enthält im Meßbereich 5 Ionisierungen (Tab. I) mit ausgeprägter Schwingungsfeinstruktur.

B. Die Pyrolysen von F_3C-N_3 und $F_3C-N=N-CF_3$

Bei Pyrolyse von F_3C-N_3 im Kurzweg-Ofen [17] des PE-Spektrometers (vgl. Exp. Teil) treten erst oberhalb 1120 K die charakteristischen N_2-Banden auf (Abb. 2: schwarz), welche die beginnende Azid-Zersetzung anzeigen. Gleichzeitig wird das Ionisationsmuster von FCN (Abb. 2) sichtbar. Bei 1270 K erfolgt die Umsetzung nahezu vollständig; Banden weiterer Produkte, insbesondere der bei 1,2-F-Wanderung (1) zu erwartenden Zwischenverbindung $F_2C=NF$ (Abb. 1) oder des stöchiometrisch erforderlichen F_2, sind nicht zu erkennen.
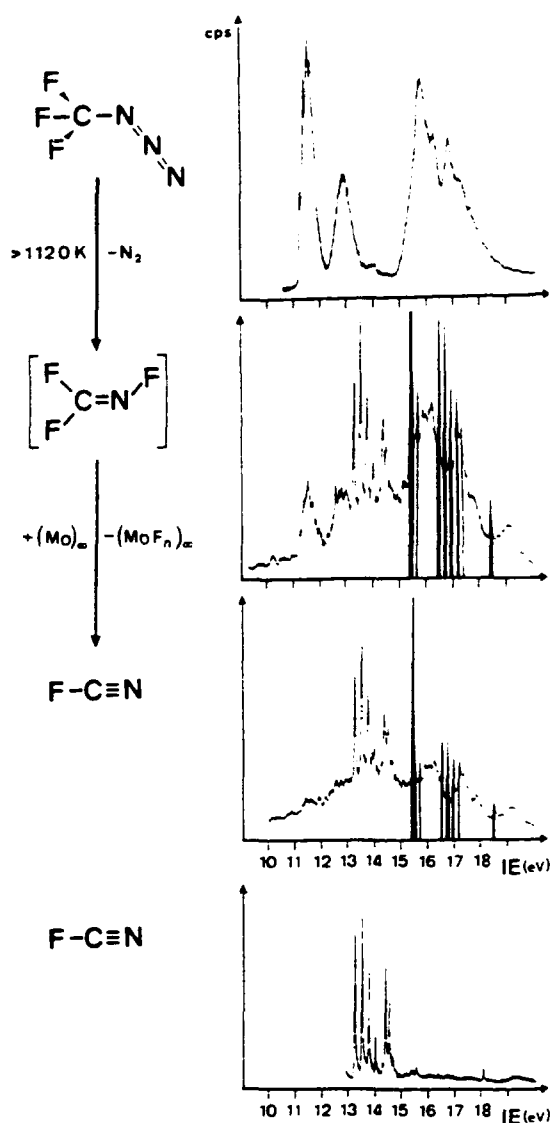
Abb. 2. He(I)-PE-Spektren von Trifluormethylazid und seiner Zersetzungsprodukte bei Pyrolyse im Kurzweg-Ofen mit Molybdän-Rohr bei 1160 K und 1270 K (vgl. Text; N_2-Banden schwarz).

Die PE-spektroskopischen Befunde lassen sich unter Annahme erklären, daß bekanntermaßen korrosive Verbindungen wie F_2 oder $F_2C=NF$ [19] die Wandung des beheizten Molybdän-Rohres fluorieren und daher für die Zersetzung von F_3C-N_3 folgende Gesamtbilanz resultiert:

$$F_3C-N_3 + (Mo)_\infty \xrightarrow{>1120\,K} N_2 + FCN + (MoF_x)_\infty \qquad (8)$$
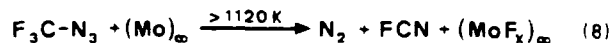
Die Pyrolyse wird daher in einem extern beheizten Quarzrohr von 20 cm Länge wiederholt. Die N_2-Ab-

spaltung beginnt bei bereits 820 K. und bei 1020 K ist F_3C-N_3 vollständig zersetzt. Es wird keine Bildung von $F_2C=NF$ oder FCN beobachtet: als Produkt ist neben N_2 unerwartet N_2O an den scharfen Nadeln bei 12.89 eV und 16.4 eV [12] nachweisbar. Des weiteren bleibt auch bei vollständiger Zersetzung von F_3C-N_3 zwischen 12.5 eV und 14 eV eine breite Bande erhalten, die das Entstehen einer weiteren Verbindung unbekannter Struktur nahelegt. Die Anwesenheit von SiF_4 im Pyrolysegemisch ist nicht auszuschließen: allerdings werden weder CO noch CO_2 beobachtet, die in der Regel bei Fluorierung von Quarz mit Fluorkohlenwasserstoffen auftreten [20].

Die beobachtete Bildung von N_2O ließe sich über einen mindestens zwei N-Atome enthaltenden Vorläufer wie Hexafluorazomethan formulieren, das analog zur bekannten Darstellung des Cyan-Derivates $NC-N=N-CN$ durch Pyrolyse von $NC-N_3$ [21] aus Trifluormethylazid nach

$$2\ F_3C-N_3 \xrightarrow[-2\,N_2]{T/SiO_2} \underset{?}{\overset{F_3C}{\diagdown}}N=N\diagdown CF_3 \qquad (9)$$
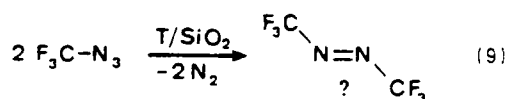
entstehen könnte. Das literaturbekannte [22] PE-Spektrum von *trans*-Hexafluorazomethan (Abb. 4) weist eine isolierte, breite Bande bei 11.50 eV auf, die der n_N-Ionisierung zugeordnet ist und die in den während der F_3CN_3-Pyrolyse registrierten PE-Spektren nicht beobachtet wird. Allerdings könnte sich $F_3C-N=N-CF_3$ unter den Pyrolyse-Bedingungen sofort weiter zersetzen, und sich so einem PE-spektroskopischen Nachweis als Zwischenprodukt entziehen. Aus diesem Grunde wird seine thermische Zersetzung (Abb. 3) zusätzlich untersucht.

Die N_2-Abspaltung aus $F_3C-N=N-CF_3$ beginnt bereits bei 870 K und erfolgt oberhalb 920 K vollständig (Abb. 3). Bei den zur Pyrolyse von F_3C-N_3 erforderlichen Temperaturen von 1120 K ist daher Hexafluorazomethan somit nicht mehr beständig. Bei seiner unter vergleichbaren Bedingungen im externen Quarzrohr mit 20 cm langer Heizzone durchgeführten Thermolyse (Abb. 3) entstehen weder N_2O noch $F_2C=NF$ oder FCN: Als Produkte werden PE-spektroskopisch außer N_2 Spuren von CO [12] sowie CO_2 [12] beobachtet, die sich bei Reaktionen von F_3C-Gruppen mit der Quarzoberfläche bilden [20]: größere Mengen SiF_4 lassen sich jedoch nicht nachweisen. Das durch Computersubtraktion der N_2-, CO- und CO_2-Banden erhaltene Spektrum des

$F_3C\diagdown N=N\diagdown CF_3$

$>870\ K\quad -N_2$

$920\ K$

F_3C-CF_3
$+CO+CO_2$

$VAX \atop 11/750$ $\begin{matrix}-N_2\\-CO\\-CO_2\end{matrix}$

(F_3C-CF_3)
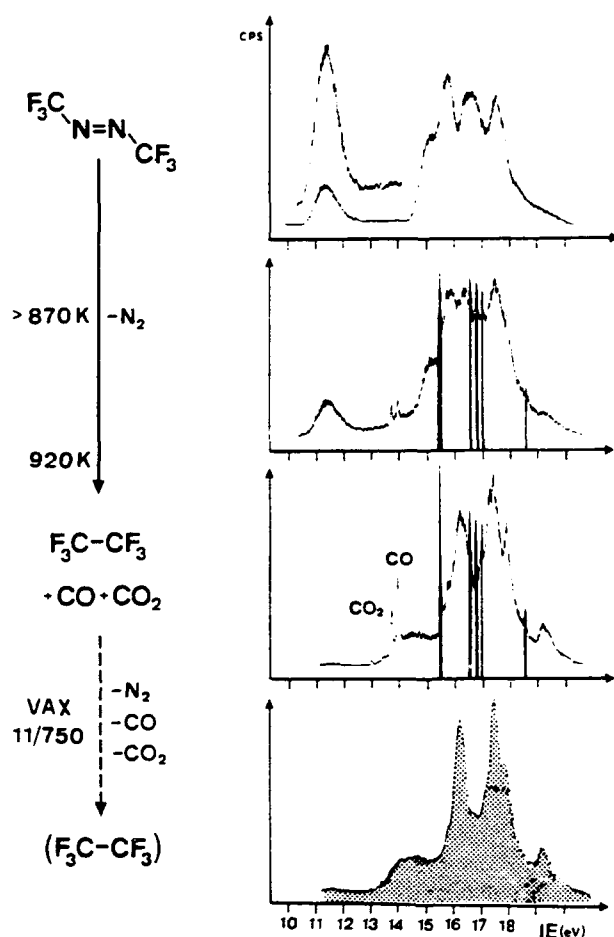
Abb. 3. He(I)-PE-Spektren von *trans*-Hexafluorazomethan und der bei Pyrolyse im externen Quarzrohr bei 880 K und 920 K entstehenden Produkte (vgl. Text, N_2-Banden schwarz). Computer-Subtraktion der Ionisationsmuster von N_2, CO und CO_2 liefert das schraffierte Spektrum, welches nach Literaturvergleich [23] Hexafluorethan zuzuordnen ist.

Hauptproduktes (Abb. 3: schraffiert) ist nach Vergleich mit dem literaturbekannten [23] PE-Spektrum Hexafluorethan zuzuordnen:

$$F_3C\diagdown N=N\diagdown CF_3 \xrightarrow{[SiO_2]} F_3C-CF_3 + N_2\ (+CO+CO_2) \qquad (10)$$
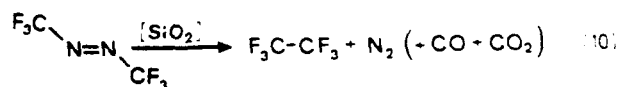
Hexafluorazomethan ist somit nicht der gesuchte N_2-Vorläufer.

Zusammenfassend ist festzuhalten: Die Pyrolyse des thermisch sehr beständigen Trifluormethylazids erfolgt erst oberhalb von 1120 K und führt − vermutlich unter Bildung von Oberflächen-Fluoriden an

der Wandung des verwendeten beheizten Molybdän-Rohres – überwiegend zu N_2 und FCN. Das bei synchroner N_2-Abspaltung und 1.2-F-Wanderung [1–4. 7] zu erwartende $F_2C=NF$ wird nicht beobachtet. Auch Quarz als Ofenmaterial ist zu seinem Nachweis ungeeignet; hier bildet sich aus F_3C-N_3 ein Gemisch gasförmiger Produkte, das unter anderem N_2 und N_2O. jedoch weder $F_2C=$ √F noch FCN als PE-spektroskopisch identifizierbare Bestandteile enthält. Des weiteren kann Hexafluorazomethan als Zwischenstufe der Pyrolyse von F_3C-N_3 ausgeschlossen werden, da seine bei 250 K niedriger Temperatur ablaufende Zersetzung unter N_2-Eliminierung zu F_3C-CF_3 führt. Die intermediäre Bildung eines Trifluormethylnitrens (F_3CN) bei der N_2-Abspaltung aus F_3CN_3 ist daher wenig wahrscheinlich; vermutlich entsteht als Zwischenprodukt zunächst $F_2C=NF$. Obwohl diese Verbindung bei Normalbedingungen in Substanz isolierbar ist, kann sie bei den hohen F_3CN-Pyrolysetemperaturen PE-spektroskopisch nicht nachgewiesen werden: Die korrosive und zusätzlich „chemisch aktivierte" Verbindung reagiert zum Endprodukt FCN weiter.

Experimenteller Teil

Trifluormethylazid wird nach [11] aus F_3C-NO (Alfa) und wasserfreiem Hydrazin [24] in abs. Methanol bei 200 K hergestellt und durch fraktioniertes Umkondensieren in einer Hochvakuum-Apparatur gereinigt; Ausb. 72% (Lit. 89%). Die Reinheitsprüfung erfolgte durch Vergleich mit einer von Dr. K. O. Christie (Rocketdyne Corp., Calif.) freund-

licherweise zur Verfügung gestellten authentischen Probe.

Photoelektronen-Spektren werden mit einem Spektrometer LEYBOLD HERAEUS UPG 200 [8] bei 10^{-4} mbar Druck und mit etwa 10^4 cps registriert; die Auflösung betrug 30 meV. Alle Spektren sind mit den Xenon- und Argon($^2P_{3/2}$)-Peaks geeicht.

Kurzweg-Pyrolyse im Molybdän-Rohr: Das PE-Spektrometer UPG 200 ist mit einem eingebauten Kurzweg-Pyrolyseofen [18] ausgestattet. Das Pyrolyserohr aus Molybdän (Länge 10 cm. Durchmesser 5 mm. Heizzone 50 mm) ist im Temperaturbereich bis 680 K widerstandsbeheizt; oberhalb 680 K wird zusätzlich eine Elektronenstoß-Heizung eingeschaltet, mit der innerhalb Minutenfrist Temperaturen bis 1500 K erreichbar sind. Der Abstand zwischen dem Ende der Pyrolyse-Zone und der Meßkammer des PE-Spektrometers beträgt nur 2 cm und es ist daher möglich, auch Verbindungen mit Lebensdauern im Bereich einiger Millisekunden zu vermessen.

Pyrolyse im Quarz-Rohr: In die Probenschleuse des UPG 200 wird ein Glasrohr mit Normschliff eingeführt, an das ein Pyrolyserohr aus Quarz (Länge 35–45 cm. Durchmesser 15 mm) angeschlossen wird. Die Beheizung erfolgt durch einen klappbaren Röhrenofen (Länge der Heizzone 30 cm. max. Temp. 1500 K).

MNDO-Rechnungen sind unter voller Geometrie-Optimierung mit dem MOPAC-Programm [25] durchgeführt worden.

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THE CHEMISTRY OF CYANOGEN FLUORIDE AND THE

N-HALODIFLUOROMETHANIMINES

A Dissertation

Presented to

the Graduate School of

Clemson University

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Doctor of Philosophy

Chemistry

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by

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ABSTRACT

The reaction of $F-C{\equiv}N$ with Br_2 and KF yields N-bromodifluoro-methanimine, $CF_2{=}NBr$ (<u>1</u>), a new imine containing a reactive nitrogen-bromine bond. (<u>1</u>) adds to carbon monoxide upon photolysis to yield $BrCF_2NCO$ and adds to fluoroolefins either thermally or photochemically to yield adducts of the form, $CF_2{=}N-CF_2CFXBr$ (X = F, Br). Pyrolysis of (<u>1</u>) at 550°C in a Pyrex flow system produces $CF_2{=}N-N{=}CF_2$ in excellent yield.

The reaction of $CF_2{=}NF$ with (<u>1</u>) over KF produces a linear adduct, $CF_3N(F)-CF{=}N-Br$, which can be annulated to the isomeric N-bromo-diazir-idine, $CF_3\overline{NCF_2}N-Br$, by treatment with CsF. The diaziridine is photo-sensitive and decomposes in sunlight to $CF_3N{=}CF_2$, Br_2 and N_2.

Fluoride-catalyzed reactions of unsaturated carbon-nitrogen com-pounds determine the relative nucleophilicity of fluorinated nitrogen-based anions. Competitive reactions of pairs of the following compounds (FCN, $CF_2{=}NF$ and $CF_3N{=}CF_2$) over KF gauge the reactivity of their respec-tive anions as follows ($CF_3NF^- > (CF_3)_2N^- >> CF_2{=}N^-$). The new com-pounds, $CF_3N(F)CN$, $CF_3N(F)-CF{=}N-CF_3$ and $CF_3\overline{NCF_2}NCF_3$, were products of the competitive reactions:

$$CF_3N{=}CF_2 \;+\; F-C{\equiv}N \;\xrightarrow{KF}\; (CF_3)_2N-C{\equiv}N \;+\; (CF_3)_2N{\diagdown}\underset{F}{C}{=}N-CF_3$$

$$CF_2{=}NF \;+\; F-C{\equiv}N \;\xrightarrow{KF}\; CF_3\underset{F}{N}-C{\equiv}N \;+\; (CF_3)_2N-C{\equiv}N$$

$$CF_2{=}NF \;+\; CF_3N{=}CF_2 \;\xrightarrow{KF}\; CF_3\underset{F}{N}{\diagdown}\underset{F}{C}{=}N-CF_3 \;+\; CF_3-N\underset{CF_2}{\diagup\diagdown}N-CF_3 \quad .$$
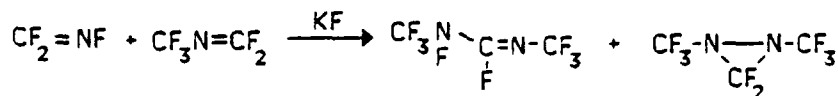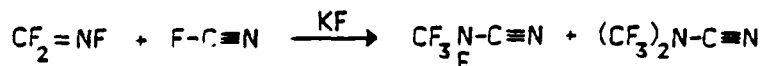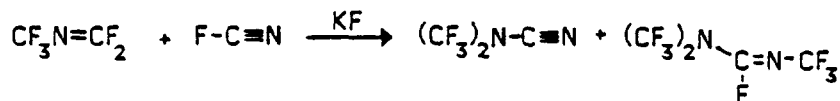
The reaction of $CF_2=NCl$ with KF or CsF and Br_2 produces a mixture of the three N,N-dihaloamines, CF_3NXX' (X,X' = Cl, Br). CF_3NBr_2 and CF_3NBrCl are extremely photosensitive, producing $CF_3N=NCF_3$ and Br_2 or BrCl, respectively.

The use of trimethylsilyl cyanide as a silylating agent for fluorinated N-bromo compounds has been explored. TMS-CN reacts with CF_3NBrF to produce $CF_3NF(TMS)$ and BrCN. TMS-CN and $CF_2=NBr$ react to produce an unstable N-silyl-imine which can be characterized by its IR spectrum in the gas phase but decomposes in condensed phases to cyanuric fluoride and TMS-F.

The addition of HF to $CF_2=NCl$ and $CF_2=NBr$ produces two unstable N-halo-trifluoromethylamines, CF_3NHCl and CF_3NHBr, which disproportionate to the N,N-dihaloamines, CF_3NCl_2 and CF_3NBr_2, respectively, and CF_3NH_2. These reactions contrast the analogous stable amine, CF_3NHF.

The reaction of the CF_3NCl_2 with triphenylphosphine in diglyme solution produces an unstable P-N species, $CF_3N=PPh_3$, which has been followed by low temperature ^{19}F and ^{31}P NMR spectroscopy. The relationship of this nitrogen system to the related carbon ylid system was investigated.

Reactions of N-Bromodifluoromethanimine[1]

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N-Bromodifluoromethanimine, CF_2=NBr, can be photolyzed in the presence of fluoroolefins CF_2=CFX to yield terminal imines CF_2=NCF$_2$CFXBr (X = F, Br) in high yields. These terminal imines can be isomerized readily by treatment with KF or CsF to the corresponding internal isomers, CF_3N=CF(CFXBr). Photolysis of CF_2=NBr at 25 °C in the presence of carbon monoxide yields bromodifluoromethyl isocyanate, BrCF$_2$N=C=O. Pyrolysis of CF_2=NBr at 550 °C yields 1,1,4,4-tetrafluoro-2,3-diazabuta-1,3-diene, CF_2=NN=CF$_2$, in excellent yield. Reaction of CF_2=NBr with CF_2=NF over KF produces a linear adduct, CF_3N(F)CF=NBr, which can be cyclized to the isomeric N-bromodiaziridine, $CF_3\overline{NCF_2NBr}$, by treatment with CsF. Seven new compounds are reported with characterization by IR, NMR, mass spectra, and physical properties. Alternative and improved syntheses of three compounds are also reported.

The perfluorinated N-haloimines, CF_2=NX (X = F, Cl, Br), provide interesting models for structural studies and an opportunity to explore the chemistry of the imine double bond and the N–X bond in an analogous series. These small molecules contain two potential reactive sites. Depending on the nature of the halogen, the N–halo bond can be the reactive link for free-radical reactions, which preserve the difluoromethylenimine functionality. On the other hand, preferential reaction of nucleophiles, especially fluoride ion, at the difluoromethylene group generates an N-halo anion, CF_3NX^-, which displays a varied reactivity depending on the halogen.

The versatile behavior of CF_2=NX (X = F, Cl) in the presence of alkali metal fluorides[2–4] and the thermolysis of the N–Cl bond in the olefin addition chemistry CF_2=NCl[5] have been described. CF_2=NX (X = F, Cl) have also been the subject of several structural studies.[6–8] For some time a method for the synthesis of CF_2=NBr remained elusive because methods similar to CF_2=NF and CF_2=NCl syntheses failed to produce this analogue. Finally, an unexpected source of FCN[9] provided an opportunity to attempt the preparation of CF_2=NBr by reaction of FCN with Br$_2$ in the presence of alkali metal fluorides.[10] This successful reaction has been refined by utilizing a more practical, large-scale source of FCN to provide useful quantities of CF_2=NBr. Studies on the reaction chemistry of CF_2=NBr have been carried out and provide interesting comparisons with known chemistry of CF_2=NF and CF_2=NCl.

Experimental Section

General Methods. All volatile materials were handled in either a stainless-steel (type 304 or 316) or glass vacuum system equipped with stainless-steel or Teflon–glass valves, respectively. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Amounts of reactants and products were measured by PVT measurements, assuming ideal gas behavior. Temperatures were measured by a digital readout iron–constantan thermocouple.

Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer with a Model 7500 data station, using a 10-cm glass cell fitted with KCl windows. ^{19}F NMR spectra were recorded on either a JEOL FX-90Q or an IBM NR200AF with CFCl$_3$ as the reference and CDCl$_3$, acetone-d_6 or benzene-d_6 as the lock solvent. Mass spectra were recorded on a Hewlett-Packard 5985-B spectrometer at 70 eV for both EI and CI (CH$_4$). Samples were introduced by direct gas injection.

Reagents. FCN was prepared by a modification of the literature technique.[11] Cyanuric fluoride (made from cyanuric chloride by the method of Tullock and Coffman[12]) was stored in a Pyrex vessel fitted with two Teflon–glass valves and containing 1 g of NaF at 0 °C. A stream of nitrogen was passed through a flow system consisting in sequence of a CaSO$_4$ drying column, a mass flowmeter, the trimer vessel, a 3 ft × $^3/_8$ in. o.d. platinum tube heated in an electric furnace to 1100 °C, and a Pyrex trap cooled to −196 °C in a hood. The flow rate was maintained at 200–500 sccm (standard cubic centimeters per minute) for 1–2 h, and in a typical run 2–5 g of (FCN)$_3$ was consumed. The products were separated by fractionation through a series of cold traps under dynamic vacuum. A −110 °C trap retained unreacted cyanuric fluoride and cyanogen. A −125 °C trap retained FCN, and a −196 °C trap collected CF$_3$CN and CF$_3$N=CF$_2$. Repeated distillation was necessary to obtain pure FCN. Yields of FCN were typically 20% while CF$_3$CN and (CN)$_2$ comprised 20–30% of the products. The balance was unreacted cyanuric fluoride and small amounts of other unidentified products.

NOTE: Cyanogen fluoride has been shown to polymerize explosively and must be handled with extreme caution. We have not experienced any explosive behavior while handling 3–30-mmol samples in glass vacuum systems at FCN pressures of less than 1 atm.

CF_2=NF[13] was prepared by a literature method. KF and CsF were activated by fusion in a platinum crucible and grinding in a ball mill under very anhydrous conditions. Other reagents were used as received or were purified by standard procedures. As necessary, product samples were further purified by GLC using a 10-ft column packed with 15–30% Halocarbon oil on Chromosorb P.

CF_2=NBr was prepared by a modification of the procedure described earlier.[10] In a typical preparation, KF (2.0 g, 34 mmol) was placed in a 100-mL two-piece Pyrex reactor joined by an Ace-Thred connector with a Viton O-ring and fitted with a Teflon–glass valve. After the vessel was evacuated, FCN and Br$_2$ (10.0 mmol each) were introduced at −196 °C by vacuum transfer. The flask was warmed to 22 °C under a stream of tap water, shaken for 3 min, and cooled to −196 °C. After removal of any noncondensible gases, the volatiles were quickly transferred from the flask to the vacuum line for trap-to-trap distillation at temperatures of −70, −120, and −196 °C. CF_2=NBr and some Br$_2$ collected at −120 °C. The −196 °C trap retained unreacted FCN (~2 mmol, 20%), which was recycled. The −70 °C trap retained CF$_3$NBr$_2$ (1.5 mmol, 15%) and Br$_2$. Pure CF_2=NBr was obtained

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by treatment with excess ethylene to remove traces of Br_2. The mixture of CF_2=NBr, $C_2H_4Br_2$, and C_2H_4 was separated by trap-to-trap distillation at temperatures of −55, −120, and −196 °C. Pure CF_2=NBr (6.0 mmol, 60% yield) collected at −120 °C.

Derivatives. CF_2=NN=CF_2. CF_2=NBr (3.7 mmol) was condensed into a 10-mL Pyrex tube fitted with a Teflon–glass valve. The vessel was then connected to a 1 in. o.d. × 3 ft Pyrex tube filled with short glass tubing sections (5 mm o.d.) which was connected to vacuum through a trap cooled to −196 °C. The packed section was heated to 550 °C, and the CF_2=NBr was slowly introduced into the system at static vacuum. After 5 min, a mixture of bromine and CF_2=N-N=CF_2 was observed in the −196 °C trap. The system was then reevacuated to remove a small amount of N_2. The contents of the −196 °C trap were treated with excess ethylene at 22 °C to remove the bromine and fractionated through a series of cold traps at −50, −120, and −196 °C. Pure CF_2=NN=CF_2 (1.78 mmol, 95% yield) collected in the −120 °C trap. Spectral data were in agreement with the literature.[14]

$BrCF_2NCO$. CF_2=NBr (1.0 mmol) and CO (6.0 mmol) were added to a 100-mL Pyrex reactor equipped with a Teflon–glass valve and cooled to −196 °C. The reactor was allowed to warm to 22 °C, and the mixture was irradiated with a 250-W medium-pressure Hg lamp for 12 h. Excess CO was removed by pumping on the flask at −196 °C. Some involatile material was not further characterized. The volatile product was chromatographed on a 15% Halocarbon oil on Chromosorb P column. The pure isocyanate was isolated in 55% yield: IR (10 torr) 3717 (w), 3253 (w), 2394 (w), 2281 (vs, N=C=O), 1454 (s, N=C=O), 1155 (vs), 1119 (vs), 975 (vs), 830 (m), 656 (w), 604 (w) cm⁻¹; MS (CI), m/z 174/172 (MH⁺), 154/152 (M − F)⁺, 146/144 (MH⁺ − CO), 131/129 (M − NCO)⁺, 109/107 (M − CF₂N)⁺, 92 (M − Br)⁺; MS (EI), m/z 154/152 (M − F)⁺, 131/129 (M − NCO)⁺, 109/107 (M − CF₂N)⁺, 92 (M − Br)⁺, 81/79 (Br⁺), 69 (CF₃⁺); ¹⁹F NMR (C_6D_6) δ −46.1 (s).

CF_2=NCF_2CF_2Br. Photolysis. Into a 100-mL Pyrex reactor fitted with a Teflon–glass valve were added CF_2=NBr (1.0 mmol) and C_2F_4 (4.0 mmol). The mixture was irradiated with a 250-W medium-pressure Hg lamp for 1 h. The product mixture was separated by trap-to-trap distillation using −85, −120, and −196 °C traps. Pure CF_2=NCF_2CF_2Br (0.8 mmol, 82% yield) collected in the −85 °C trap. Some involatiles were left in the reaction vessel, which were not identified further.

Thermolysis. With the same reactor as above, the two reactants (1.0 mmol of CF_2=NBr, 4.0 mmol of C_2F_4) were heated in a water bath at 95 °C for 8 h. The yield of CF_2=NCF_2CF_2Br was 67%. The remainder of the starting material was consumed in involatile side product formation. IR (8 torr) 1799 (C=N, vs), 1317 (vs), 1288 (s), 1243 (vs), 1179 (vs), 1110 (s), 984 (s), 905 (s), 879 (s), 807 (m), 775 (m) cm⁻¹; MS (CI, major), m/z 246/244 (MH⁺, 100), 226/224 (M − F)⁺, 181/179 (M − CF₂N)⁺, 164 (M − Br)⁺, 131/129 (CF₂Br)⁺, 114 (CF₂CF₂N)⁺; MS (EI), m/z 245/243 (M)⁺, 226/224 (M − F)⁺, 181/179 (M − CF₂N)⁺, 176/174 (M − CF₃)⁺, 164 (M − Br)⁺, 145 (M − BrF)⁺, 131/129 (CF₂Br)⁺, 114 (CF₂CF₂N⁺, 100), 100 (CF₂CF₂)⁺, 95 (CF₂NCF)⁺, 81/79 (Br)⁺, 69 (CF₃)⁺; ¹⁹F NMR (C_6D_6) (F^AF^BC=$NCF_2^NCF_2^MBr$) δ −27.7 (br d, A), −43.4 (br d, B), −69.2 (m, N), −93.3 (m, M), J_{AB} = 88 Hz, $J_{AM} \simeq J_{BM} \simeq$ 2 Hz, J_{AN} = J_{BN} = 11 Hz, J_{MN} = 3 Hz.

CF_2=NCF_2CFBr_2. CF_2=NBr (2.0 mmol) and CF_2=CFBr (6.0 mmol) were added to a 100-mL Pyrex reactor and irradiated with a medium-pressure Hg lamp for 3 h. The volatiles were separated through traps at −70, −120, and −196 °C. Pure CF_2=NCF_2CFBr_2 (1.3 mmol, 65% yield) was isolated in the −70 °C trap. Some involatile material remained in the reactor. IR (10 torr) 1798 (C=N, vs), 1314 (vs), 1249 (vs), 1205 (vs), 1154 (vs), 1098 (vs), 1060 (m), 991 (m), 971 (m), 871 (s), 826 (vs), 771 (s), 728 (m), 605 (w) cm⁻¹; MS (CI, major), m/z 308/306/304 (MH⁺), 307/305/303 (M⁺), 288/286/284 (M − F)⁺, 266/264/262, 243/241/239 (M − CF₂N)⁺, 226/224 (M − Br)⁺, 204/202 (M − BrF)⁺, 193/191/189 (CFBr₂)⁺; MS (EI), m/z 243/241/239 (M − CF₂N)⁺, 226/224 (M − Br)⁺, 204/202 (M − BrF)⁺, 193/191/189 (CFBr₂)⁺; ¹⁹F NMR (C_6D_6) (F^AF^BC=$NCF_2^NCF^MBr_2$) δ −28.2 (br d, A), −44.1 (br d, B), −73.2 (m, M), −89.4 (m, N), J_{AB} = 88 Hz, J_{AN} = J_{BN} = 11 Hz, J_{MN} = 14 Hz, J_{AM} = J_{BM} = 2 Hz.

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CF_3N=$CFCF_2Br$ and CF_3N=$CFCFBr_2$. Exposure of C-F_2=NCF_2CF_2Br and CF_2=NCF_2CFBr_2 to KF for 1 h or CsF for 15 min converted the terminal imines to the internal isomers. CF_3N=$CFCF_2Br$ and CF_3N=$CFCFBr_2$, respectively, in essentially quantitative yields.

CF_3N=$CFCF_2Br$: bp 54.2 °C; mp <−125 °C; log P (torr) = 7.1565 − (1399.8/T), ΔH_{vap} = 6.40 kcal/mol, ΔS_{vap} = 19.6 eu: IR (8 torr) 1771 (vs, C=N), 1316 (s), 1254 (vs), 1209 (vs), 1133 (m), 1105 (s), 1020 (w), 962 (s), 819 (s), 774 (m), 655 (m), 624 (m) cm⁻¹; MS (CI, major), m/z 246/244 (MH⁺), 245/243 (M⁺), 226/224 (M − F)⁺, 181/179 (C₂F₄Br)⁺, 164 (M − Br)⁺, 131/129 (CF₂Br)⁺, 114 (C₂F₄N)⁺; MS (EI), m/z 245/243 (M)⁺, 226/224 (M − F)⁺, 181/179 (CF₂F₄Br)⁺, 174 (M − CF₃)⁺, 164 (M − Br)⁺, 145 (M − BrF)⁺, 131/129 (CF₂Br)⁺, 119 (C₂F₅)⁺, 114 (C₂F₄N)⁺, 100 (C₂F₄)⁺, 95 (CF₃NC)⁺, 69 (CF₃)⁺; ¹⁹F NMR (C_6D_6) (CF_3^MN=$CF^ACF_2^XBr$, AM_3X_2 spin system) δ −32.1 (br d, A), −57.2 (d, M), −61.6 (m, X), J_{AM} = 10.2 Hz, J_{AX} = 7.6 Hz, $J_{MX} \leq$ 1.0 Hz.

CF_3N=$CFCFBr_2$: IR (9 torr) 1759 (vs, C=N), 1282 (vs), 1255 (vs), 1201 (vs), 1128 (s), 909 (w), 839 (w), 812 (m), 794 (s), 778 (m), 750 (w), 680 (m), 618 (m) cm⁻¹; MS (CI, major), m/z 308/306/304 (MH)⁺, 307/305/303 (M)⁺, 288/286/284 (M − F)⁺, 243/241/239 (M − CF₂N)⁺, 227/225 (MH − Br)⁺, 226/224 (M − Br)⁺, 207/205 (M − BrF)⁺, 193/191/189 (CFBr₂)⁺, 176/174 (M − CF₂Br)⁺, 131/129 (CF₂Br)⁺, 114 (CF₃NCF)⁺; MS (EI), m/z 243/241/239 (M − CF₂N)⁺, 226/224 (M − Br)⁺, 207/205 (M − BrF)⁺, 193/191/189 (CFBr₂)⁺, 176/174 (M − CF₂Br)⁺, 162/160 (C₂F₃Br)⁺, 145 (M − 2Br)⁺, 131/129 (CF₂Br)⁺, 114 (CF₃NC)⁺, 112/110 (CFBr)⁺, 81/79 (Br)⁺, 77 (C₂F₂NH)⁺, 76 (C₂F₂N)⁺, 69 (CF₃)⁺; ¹⁹F NMR (C_6D_6) (CF_3^MN=$CF^ACF^NBr_2$, AM_3N spin system) δ −30.2 (dq, A), −56.6 (d, M), −68.6 (d, N), J_{AM} = 13 Hz, J_{AN} = 24 Hz, J_{MN} = 2 Hz.

$CF_3N(F)CF$=NBr. KF (1.0 g, 17 mmol) was added to a two-piece 100-mL Pyrex reactor with an Ace-Thred connector with Viton O-ring and a Teflon–glass valve. The reactor was evacuated and cooled to −196 °C. CF_2=NF (1.0 mmol) and CF_2=NBr (2.5 mmol) were added to the reactor, allowed to warm to 22 °C, and stirred for 5 h. Vacuum fractionation of the volatiles gave a mixture of $CF_3N(F)CF$=NBr and CF_2=NBr in the −80 °C trap and CF_2=NBr in the −196 °C trap. The mixture was purified by repeated dynamic distillation through a −105 °C trap to remove the more volatile CF_2=NBr. $CF_3N(F)CF$=NBr (0.5 mmol) was isolated in 50% yield based on starting CF_2=NF. (The dimer of CF_2=NF, $CF_3N(F)CF$=NF, and CF_3NBrF were not identified as side products, although these compounds comprise likely sources of yield losses.) IR (8 torr) 1688 (C=N, vs), 1295 (vs), 1245 (vs), 1213 (vs), 1167 (vs), 994 (m), 815 (w), 711 (m) cm⁻¹; MS (CI, major), m/z 229/227 (MH⁺), 228/226 (M⁺), 210/208 (MH − F)⁺, 209/207 (M − F)⁺, 148 (MH − Br)⁺, 127/125 (CFNBr)⁺; MS (EI, major), m/z 228/226 (M)⁺, 147 (M − Br)⁺, 126/124 (CFNBr)⁺, 81/79 (Br⁺), 69 (CF₃)⁺; ¹⁹F NMR (C_6D_6) (CF_3^NN-(F^A)CF^M=NBr, AMN_3 spin system) δ −26.6 (dq, A), −60.8 (dq, M), −70.1 (dd, N), J_{AM} = 38.3 Hz, J_{MN} = 15.5 Hz, J_{AN} = 8.4 Hz.

$\overline{CF_3NCF_2NBr}$. $CF_3N(F)CF$=NBr (0.5 mmol) was condensed into a 100-mL Pyrex reactor previously charged with 0.9 g (6 mmol) of CsF. After stirring for 20 min at 22 °C, the volatiles were fractionated through a −70 °C trap to remove a small amount of CF_3NBr_2. The −196 °C trap contained 0.46 mmol of $\overline{CF_3N-CF_2NBr}$ (92% yield based on starting $CF_3N(F)CF$=NBr): IR (10 torr) 1414 (s), 1382 (m), 1294 (vs), 1229 (vs), 1049 (m), 940 (m), 829 (w), 677 (m), 658 (s) cm⁻¹; MS (CI, major), m/z 229/227 (MH)⁺, 228/226 (M)⁺, 215, 213, 209/207 (M − F)⁺, 149 (M + 2H − Br)⁺, 148 (MH − Br)⁺, 147 (M − Br)⁺, 134 (MH − NBr)⁺, 131/129 (CF₂Br)⁺, 128 (C₂F₄N₂)⁺, 114 (C₂F₄N)⁺; MS (EI), m/z 147 (M − Br)⁺, 131/129 (CF₂Br)⁺, 128 (C₂F₄N₂)⁺, 114 (C₂F₄N)⁺, 109 (CF₃N₂C)⁺, 95/93 (NBr)⁺, 81/79 (Br)⁺, 69 (CF₃)⁺, 50 (CF₂)⁺; ¹⁹F NMR (C_6D_6) ($CF_3^ANCF^MF^NN$-Br, A_3MN spin system) δ −64.0 (dd, A), −100.5 (br d, M), −112.9 (dq, N), J_{MN} = 32.2 Hz, J_{AN} = 11.2 Hz, J_{AM} = 2.4 Hz.

Results and Discussion

The pyrolysis of cyanuric fluoride in Pt at 1100 °C provides a simple means of obtaining useful quantities of FCN. The much more elaborate apparatus employed by

Scheme I

overall reaction steps

$$R_fCF{=}NBr \xrightarrow{h\nu} R_fCF{=}N{\diagdown}_{N=CFR_f}$$

$$R_f = CF_3, \ C_2F_5, \ n\text{-}C_3F_7$$

$$R_fCF{=}NBr \xrightarrow{h\nu} R_fCF{=}N^{\bullet} + Br^{\bullet}$$

$$R_fCF{=}N^{\bullet} {\left\{\begin{array}{l} FC{\equiv}N + R_f^{\bullet} \\ R_fCF{=}N{\diagdown}_{N=CFR_f} \end{array}\right.}$$

$$2Br^{\bullet} \longrightarrow Br_2$$

Fawcett and Lipscomb gave higher yields at an optimum temperature of ~1300 °C.[11] However, their work implies that temperatures in excess of 1200 °C are needed for good yields, thus requiring an expensive resistively heated furnace or induction heating. In our work, the 1100 °C temperature is easily obtainable with inexpensive commercial tube furnaces and the lower temperature raises the possibility of using a much less expensive material than Pt for the pyrolysis tube.

The preparation of $CF_2{=}NBr$ in small-batch reactions was greatly improved over that previously reported[10] by using short reaction times and stoichiometric amounts of Br_2. Even then, it is impossible to suppress the further oxidation of $CF_2{=}NBr$ to CF_3NBr_2, which clearly occurs at a rate comparable to that of forming $CF_2{=}NBr$:

$$FCN \xrightarrow[MF]{Br_2} CF_2{=}NBr \xrightarrow[MF]{Br_2} CF_3NBr_2$$

The maximum yields of $CF_2{=}NBr$ under conditions described in the Experimental Section are ~75% with an ~80% conversion of FCN to products.

In exploring the chemistry of $CF_2{=}NBr$, our interest was to compare the reactivity of the analogous series of $CF_2{=}NX$ and to compare $CF_2{=}NBr$ with other N-bromoimines of the type $R_fCF{=}NBr$. The thermolysis or photolysis of $CF_2{=}NF$ or $CF_2{=}NCl$ is not a practical route to the azine because of the harsh conditions necessary to cleave the N–F or N–Cl bond. Thermolysis of $R_fCF{=}NBr$ gave decomposition rather than the azines, while photolysis readily produced the respective azines as shown in Scheme I.[9] Pyrolysis of $CF_2{=}NBr$ readily produced the azine $CF_2{=}NN{=}CF_2$ in a unique reaction for the perfluoro N-haloimines. This azine was first prepared by photolysis of difluorodiazirine and later by the AgF fluorination of the tetrabromo analogue $Br_2C{=}NN{=}CBr_2$.[14,15] Both prior methods are difficult to execute, and the two-step conversion from FCN to $CF_2{=}NN{=}CF_2$ is clearly superior.

$$F_2C{\diagup\!\!\!\!\diagdown}^{N}_{N} \xrightarrow{h\nu} F_2C{=}N{\diagdown}_{N=CF_2}$$

$$Br_2C{=}N{\diagdown}_{N=CBr_2} \xrightarrow{AgF} F_2C{=}N{\diagdown}_{N=CF_2}$$

$$2F_2C{=}NBr \xrightarrow{\Delta} F_2C{=}N{\diagdown}_{N=CF_2}$$

The synthesis of $BrCF_2NCO$ by the addition of CO to $CF_2{=}NBr$ is analogous to the thermal reaction of CO with other perfluoroalkyl N-bromoimines, which produced a series of α-bromo isocyanates.[16] Scheme II illustrates the scope of the previous reaction and includes the $CF_2{=}NBr$

Scheme II

overall reaction steps

$$\begin{array}{c}R_x\\ \diagdown\\ F\end{array}{C}{=}N{\diagdown}_{Br} + CO \xrightarrow[\text{or } h\nu]{\Delta} \begin{array}{c}R_x\\ \diagdown\end{array}{C}{\diagup}^{F}_{N=C=O}{\diagdown}_{Br}$$

$$R_x = CF_3, \ C_2F_5, \ CCl_3 \ (\Delta); \ F \ (h\Delta)$$

$$\begin{array}{c}R_x\\ \diagdown\\ F\end{array}{C}{=}N{\diagdown}_{Br} \xrightarrow[\text{or } h\nu]{\Delta} \begin{array}{c}R_x\\ \diagdown\\ F\end{array}{C}{=}N^{\bullet} + Br^{\bullet}$$

$$\begin{array}{c}R_x\\ \diagdown\\ F\end{array}{C}{=}N^{\bullet} + CO \longrightarrow \begin{array}{c}R_x\\ \diagdown\\ F\end{array}{C}{=}N{\diagdown}_{\overset{\bullet}{C}=O}$$

$$\begin{array}{c}R_x\\ \diagdown\\ F\end{array}{C}{=}N{\diagdown}_{\overset{\bullet}{C}=O} \longrightarrow \begin{array}{c}R_x\\ \diagdown\end{array}{C}{\diagup}^{F}_{N=C=O}{\diagdown}_{\overset{\bullet}{}}$$

$$\begin{array}{c}R_x\\ \diagdown\end{array}{\overset{\bullet}{C}}{\diagup}^{F}_{N=C=O} + Br^{\bullet} \longrightarrow \begin{array}{c}R_x\\ \diagdown\end{array}{C}{\diagup}^{F}_{N=C=O}{\diagdown}_{Br}$$

Scheme III

$$CF_2{=}NB{\cdot} \xrightarrow[\text{or } \Delta]{h\nu} CF_2{=}N^{\bullet} + Br^{\bullet}$$

$$CF_2{=}N^{\bullet} + CF_2{=}CX_2 \longrightarrow CF_2{=}NCF_2CX_2^{\bullet}$$

$$CF_2{=}NCF_2CX_2^{\bullet} \xrightarrow{CF_2=NBr} CF_2{=}NCF_2CX_2Br$$

Scheme IV

initiation

$$CF_2{=}NX \xrightarrow{\Delta} CF_2{=}N^{\bullet} + X^{\bullet}$$

propagation

$$CF_2{=}N^{\bullet} + C_2F_4 \longrightarrow CF_2{=}NCF_2CF_2^{\bullet}$$

$$CF_2{=}NCF_2CF_2^{\bullet}$$

propagation | termination

$$nC_2F_4 \qquad\qquad CF_2{=}NX$$

$$CF_2{=}N(CF_2CF_2)_nX \qquad CF_2{=}NCF_2CF_2X + CF_2{=}N^{\bullet}$$

example from this work. A proposed free-radical mechanism is also described.

Perfluoro imino radicals, $R_fCF{=}N^{\bullet}$, react with carbon monoxide differently than the saturated, bis(trifluoromethyl)aminyl, $(CF_3)_2N^{\bullet}$, which was generated from $(CF_3)_2NBr$.[17]

$$(CF_3)_2NBr + CO \xrightarrow{h\nu} (CF_3)_2NC(O)Br$$

$$CF_2{=}NBr + CO \xrightarrow{h\nu} BrCF_2N{=}C{=}O$$

The addition of $CF_2{=}NBr$ to fluoroolefins of the type $CF_2{=}CFX$ (X = F, Br) occurs regiospecifically and is also best explained by a free-radical chain mechanism (see Scheme III). The best conditions for the additions consist of photolysis of a Pyrex vessel for 1–4 h or heating at 95–125 °C for 0.5–2 days. The regiospecificity of these additions are reminiscent of the earlier $CF_2{=}NCl$ additions.[5] $SF_2{=}NX$ (X = Cl, Br) exhibit similar additions to olefins.[16] For example, $SF_2{=}NBr$ adds to C_2F_4 to give both a monoadduct, $SF_2{=}NCF_2CF_2Br$ (95%), and an oligomeric product, $SF_2{=}N(CF_2)_4Br$.[18]

In comparing the olefin addition chemistry of the series of N-haloimines, CF_2NX (X = F, Cl, Br), a systematic

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Table I

	I	II	III	IV
IR(cm^{-1})	1458	1414	1420	1410
^{19}F NMR chemical shifts (ppm, rel CFCl$_3$)	A -67.9 M -91.8 N -108.1	A -12.4 M -62.9 X -111.8 Y -113.1	A -64.9 M -106.3 N -112.4	A -64.0 M -100.5 N -112.9
coupling constants (Hz)	J_{AM} = 3.1 J_{MN} = 1.8 J_{AN} = 15.8	$J_{AM} \leq 2$ J_{AX} = 17.5 J_{AY} = 9.5 J_{XY} = 41.5 $J_{MX} \leq 2$ J_{MY} = 9.5	J_{AM} = 32.5 J_{AN} = 12.0 J_{MN} = ≤ 2	J_{AM} = 2.4 J_{AN} = 11.2 J_{MN} = 32.2

trend in radical chain mechanism which varies with the bond strength of the initiator (in this case, the homolyzed N–X bond) is observed in the distribution of monoadduct and polymeric products. In order to propagate an olefin polymerization reaction, the initiator bond must be reasonably strong.[19] Likewise, a weak bond in the initiator will favor chain transfer after only one unit of olefin has been added. As shown in Scheme IV, the fate of the monoadduct radical is determined by the strength of the initiator bond in CF$_2$=NX.

For a strong N–X bond (i.e., CF$_2$=NF), thermal reaction with C$_2$F$_4$ gives polymerization of the olefin with little consumption of CF$_2$=NF.[20] In the case of the thermal reaction of CF$_2$=NCl with C$_2$F$_4$, isolation of a moderate yield of the monoadduct, CF$_2$=NCF$_2$CF$_2$Cl, with some additional polymeric material and unreacted CF$_2$=NCl confirms the lower bond strength of the N–Cl compound. In this work, homolysis of the N–Br bond was achieved either by mild thermal means or brief photolysis because of a much weaker N–X bond. The major products for reactions of CF$_2$=NBr with olefins were monoadducts; little polymeric material was observed and no unreacted CF$_2$=NBr was recovered. Thus, the strength of the N–X bonds in these N-haloimines correspond nicely with their respective behavior in the addition to fluoroolefins. The observed regioselectivity supports the participation of a free-radical chain mechanism.

The isomerization of fluorinated terminal imines by KF or CsF has been well studied.[21,22] Quantitative yields of rearranged imines were obtained for the aforementioned adducts, CF$_2$=NCF$_2$CFBrX (X = F, Br). This fluoride-promoted isomerization or 1,3-fluoride shift is not easily reversed because of the thermodynamic stability of the internal imine.

$$CF_2=NCF_2R_f \xrightarrow{F^-} CF_3-\bar{N}-CF_2R_f \xrightarrow{-F^-} CF_3N=C\begin{smallmatrix}F\\R_f\end{smallmatrix}$$
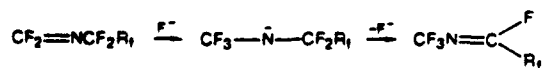
The reaction of CF$_2$=NF with CF$_2$=NBr over active alkali metal fluorides is related mechanistically to the known dimerization of CF$_2$=NF over KF and CsF.[3] The proposed mechanism for the formation of the CF$_2$=NF dimers involves nucleophilic attack of the CF$_3$NF$^-$ anion on the terminal difluoromethylene group of CF$_2$=NF with elimination of fluoride. Attack on the imino carbon of this linear dimer by a strong fluoride base (i.e., CsF) generates
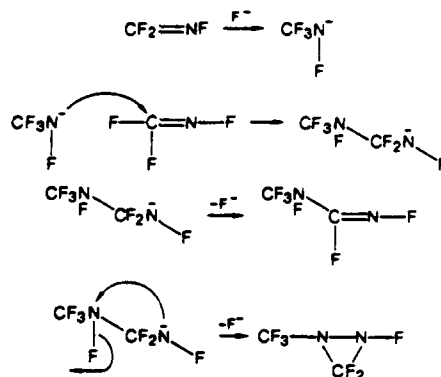
a new nitrogen anion which intramolecularly displaces fluoride from the N–F center (Scheme V).

The reaction of CF$_2$=NF with CF$_2$=NCl over CsF produced an N-chlorodiaziridine[5] and the availability of CF$_2$=NBr made the N-bromodiaziridine a logical target. The first attempt to combine CF$_2$=NF and CF$_2$=NBr over CsF produced only CF$_3$NBrF, presumably because of the decomposition of CF$_2$=NBr or its anion, CF$_3$NBr$^-$, in the presence of CsF and the strongly nucleophilic Cs$^+$CF$_3$NF$^-$.

The use of KF as catalyst allowed the isolation of the linear codimer CF$_3$N(F)CF=NBr. The brief exposure of this N-bromoimine to CsF effected the desired cyclization to the N-bromodiaziridine. Scheme VI depicts the proposed mechanism for the general two-step conversion of N-substituted imines to N-substituted (trifluoromethyl)-diaziridines. (The synthesis of the bis(trifluoromethyl)-diaziridine will be reported separately.[23]) Like the other N-halodiaziridines, the N-bromodiaziridine is observed only when CsF is used as the catalyst for the cyclization.

Although CF$_2$=NBr is only slightly sensitive to ultraviolet light, the new diaziridine contains a very reactive N–Br linkage. Exposure to Pyrex-filtered sunlight decomposed the diaziridine according to the equation shown below:

Scheme V
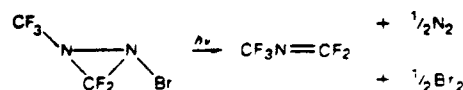
CF$_3$N=CF$_2$ is a common decomposition sink for derivatives of this ring system.[4]

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Scheme VI

X = F, Cl, Br, CF₃
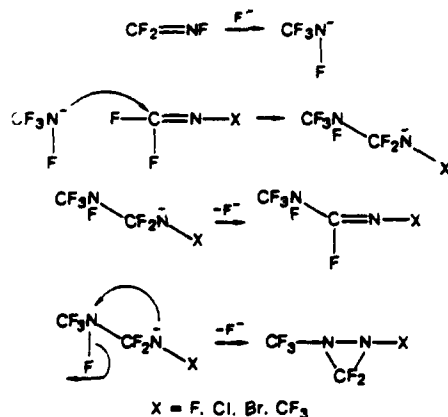
A comparison of the spectral properties of the N-halo-diaziridines prepared from CF₂=NF, CF₂=NCl, and CF₂=NBr and an analogous (trifluoromethyl)oxaziridine is provided in Table I. The characteristic ring vibration for small heterocyclic rings is observed between 1400 and 1440 cm⁻¹ for each diaziridine and at 1458 cm⁻¹ for the oxaziridine.[3,5,24] These frequencies are within the range expected for analogous fluorinated heterocycles.[25,26]

The ¹⁹F NMR spectra are instructive regarding the probable structures of these rings. The N-fluorodiaziridine serves as a model from which the other structures can be reasonably assigned. As discussed in a previous report,[3] the fluorine on nitrogen provides a probe into the relative position of the other fluorines above and below the ring plane in the N-fluorodiaziridine. Since two distinct signals are observed for the geminal fluorines on the ring carbon, the inversion of the ring can be assumed to be slow on the NMR time scale. Likewise, the geminal fluorines are nonequivalent in the N-chloro- and N-bromodiaziridines.

Assignment of the position of the trifluoromethyl group in the N-F ring was deduced according to the relative coupling constants, since each coupling constant is measurable and distinct in this system. Close proximity in space generally renders a large coupling in rigid systems in the ¹⁹F NMR.[27] According to this tenet, the trifluoromethyl group and the ring N-F were assigned as trans.[3] A cis orientation would show a large coupling constant, which is consistent with the coupling of the CF₃ group with the upper geminal fluorine (J_{MY} = 9.5 Hz) and the N-F with the lower geminal fluorine (J_{AX} = 17.5 Hz).

Diaziridines generally favor a trans arrangement of nitrogen substituents to alleviate repulsion of the two neighboring lone pairs.[28] Some diaziridines as well as triaziridines have been synthesized that can be isolated either as a cis isomer or as a mixture of isomers.[29,30] The NMR evidence favors a locked trans geometry for the N-fluorodiaziridine and it is reasonable to assume that the N-chloro- and N-bromodiaziridines have similar geometries in the absence of more definitive structure determinations.

In summary, CF₂=NBr provides many possibilities for additions in thermal and photochemical reactions as evidenced by its additions to fluoroolefins and carbon monoxide and its pyrolysis. Reaction with CF₂=NF over KF and CsF affirms the nucleophilicity of the CF₃NF⁻ anion on terminal difluoromethylene centers while indicating the poor nucleophilicity of the CF₃NBr⁻ anion. These two modes of reactivity make CF₂=NBr an attractive starting material for the synthesis of novel small molecules with potentially reactive centers.

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Microwave spectrum, quadrupole coupling constants, and structure of N–bromodifluoromethanimine

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A continuous flow system has been used to measure the microwave spectrum (26.5 to 40.0 GHz) of rapidly decomposing N–bromodifluoromethanimine, CF_2=NBr. The hyperfine structure of the spectrum caused by two nuclei with nuclear quadrupole moments (^{14}N,[79]Br, or [81]Br) has been analyzed and rotational, centrifugal distortion, and quadrupole coupling constants have been determined by a global least-squares fit for both bromine isotopic species. Identification and assignment of R transitions in the b-type spectrum have been facilitated considerably by the determination of the magnitude of the rotational constants from the hyperfine structure of the Q transitions alone. A structure compatible with the observed rotational constants has been determined for this planar molecule.

INTRODUCTION

During the last decade, new synthetic methods have made the halogenated methanimines more accessible to structural studies. The infrared spectrum of N–chlorodifluoromethanimine, CF_2=NCl, was reported[1] in 1971 but the first structural information has been obtained only recently from the analysis of the microwave spectrum.[2,3] Perfluoromethanimine, CF_2=NF, has been studied by vibrational and rotational spectroscopy and the r_a^0 structure has been derived from microwave and electron diffraction data.[4,5] The structure of perchloromethanimine, CCl_2=NCl, has been determined from electron diffraction data alone.[6] N–bromodifluoromethanimine, CF_2=NBr, has been prepared and its vibrational spectrum assigned.[7] A decomposition product of both CF_2=NCl and CF_2=NBr has been identified by its microwave spectrum as difluoromethanimine, CF_2=NH.[8] A simultaneous but independent investigation of its rotational spectrum[9] followed the recent direct synthesis of this simple imine.[10]

N–bromodifluoromethanimine is the first small molecule synthesized which contains a bond between a bromine atom and an imine nitrogen atom. The only other molecule with a Br–N=C moiety which has been studied by microwave spectroscopy is bromine isocyanate, BrN=C=O.[11] Our interest in the structural properties of such a N–bromoimine prompted us to initiate an investigation of the rotational spectrum of CF_2=NBr. The additional challenges of the chemical reactivity of this compound and of the presence of two nuclei with nuclear quadrupole moments causing extended hyperfine splittings were eventually overcome and the results are presented herein.

EXPERIMENTAL

N–bromodifluoromethanimine was synthesized by the method described by O'Brien et al.[7] It was purified by trap-to-trap distillation and stored in glass sample tubes immersed into liquid nitrogen. The first attempts to measure its microwave spectrum were unsuccessful because of the rapid decomposition of the sample in the Stark cells. The primary decomposition product was eventually identified as difluoromethanimine, CF_2=NH.[8] In the unconditioned cells, CF_2=NBr decayed completely within 1 to 2 min. The half-life of CF_2=NBr in the well conditioned Stark cells after four days of measurements with the flow-through system was about 10 to 15 min.

The microwave spectrum between 26.5 and 40.0 GHz was measured on a Hewlett–Packard model 8460 A MRR spectrometer with 33.3 kHz Stark modulation. The Stark cells were cooled with a packing of Dry Ice. Because of rapid decomposition of the sample in the Stark cells, the sample was continuously evaporated into the cells from a reservoir kept at − 80 °C while a sample tube cooled by liquid nitrogen served as the pump of the flow-through system. Precise frequencies were obtained by averaging the measurements of scans in both directions, made at sample pressures of 2 to 5 mTorr. The bandwidths at half-height were below 0.2 MHz for isolated bands. The precision and accuracy of the measurements were estimated to be about 0.02 MHz for well resolved bands.

RESULTS

Assignment of the microwave spectrum

For the initial predictions of the rotational spectrum of CF_2=NBr, a structure was assumed which was, except for the N–halogen distance, almost identical to the structure reported for CF_2=NCl.[3] The N–Br distance of 1.85 Å was transferred from the structure of Br–NCO.[11] The predicted spectrum contained, besides the expected a-type R transitions, several series of b-type Q transitions. The most intense of these, $J_{3,J-3} - J_{2,J-2}$, $J = 21, \cdots 30$, was predicted to have a bandhead near 37.2 GHz for both isotopic species of bromine (Fig. 1). The b-type Q transitions in the spectrum of CF_2=NCl investigated earlier[3] were considerably more intense than any of the R transitions. Because we assumed that
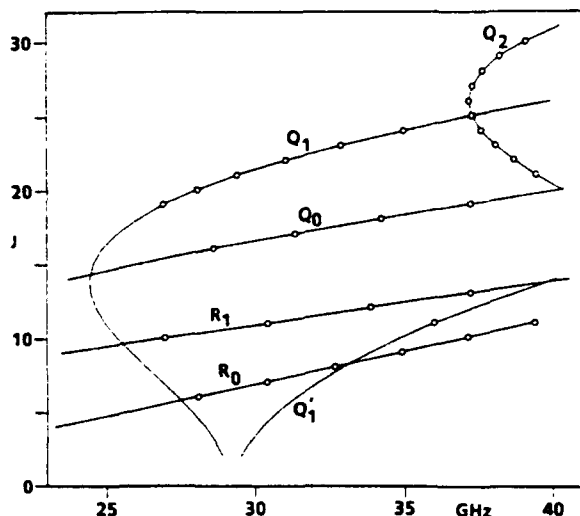
FIG. 1. $CF_2={}^{14}N^{79}Br$. Fortrat diagram of the b-type transition series $J_{1,J-1}-J_{0,J}(Q_0)$, $J_{2,J-2}-J_{1,J-1}(Q_1)$, $J_{3,J-3}-J_{2,J-2}(Q_2)$, $J_{2,J-1}-J_{1,J}(Q_1')$, $J+1_{1,J+1}-J_{0,J}(R_0)$, and $J+1_{0,J+1}-J_{1,J}(R_1)$. Open circles indicate measured transitions.

the orientation of the molecular electric dipole moment in the principal axes system was similar in $CF_2=NCl$ and $CF_2=NBr$, we expected a large number of strong absorption lines between 37.2 and 37.5 GHz. Accordingly, we started the search for the spectrum of $CF_2=NBr$ in this region.

At first, we monitored the intensity of a line of the decomposition product $CF_2=NH$ until it had decreased significantly under the continuous flow system. Then we scanned the spectral region of interest repeatedly and indeed found several lines growing in. Eventually, numerous lines between 37 and 40 GHz were observed whose intensity increased with time. Preliminary least-squares fits to the spectrum of an asymmetric rotor confirmed that these lines could be assigned to the Q transition series $J_{3,J-3}-J_{2,J-2}$ of two different molecules or states with about equal relative intensities. Eventually, the states were identified as the vibrational ground states of both bromine isotopic species of $CF_2=NBr$. All of these lines were split into several components. The observed splitting patterns agreed qualitatively with the hyperfine structure predicted with estimates of the quadrupole coupling constants for the bromine isotopes (see the next section). Subsequently, the b-type Q transitions $J_{2,J-2}-J_{1,J-1}$, $J = 19,\cdots25$ and $J_{1,J-1}-J_{0,J}$, $J = 16,\cdots19$, with considerably larger hyperfine splittings could be identified. A weaker satellite accompanied each component of these transitions at a separation of less than 1

MHz. Such an additional hyperfine splitting due to the nuclear quadrupole moment of ^{14}N had also been observed for most b-type transitions in the spectrum of $CF_2=NCl$.[3]

The assignment of R transitions was not as easy because they were considerably weaker. Q transitions usually provide only accurate differences between rotational constants but not absolute magnitudes. However, the detailed analysis of the hyperfine structure of the Q transitions of $CF_2={}^{14}N^{79}Br$ provided rather accurate estimates of the magnitudes of all rotational constants (see the next section). With these estimates, the frequencies of R transitions and their hyperfine splitting patterns were predicted. Two series of b-type R transitions, $J+1_{0,J+1}-J_{1,J}, J = 10,\cdots13$ and $J+1_{1,J+1}-J_{0,J}, J = 6,\cdots11$, could be assigned quickly for this isotope. The largest deviation from the predicted position was about 39 MHz for $J = 13$. No a-type R transitions could be observed presumably due to insufficient intensity.

The assignment of the spectrum of the second isotopic species, $CF_2={}^{14}N^{81}Br$, was straightforward. The A rotational constant was transferred from the final analysis of the spectrum of $CF_2={}^{14}N^{79}Br$, because both Cl isotopic species of $CF_2={}^{14}NCl$ had almost identical A constants.[3] Initial quadrupole coupling constants for ^{81}Br were obtained by multiplying the corresponding constants determined for $CF_2={}^{14}N^{79}Br$ with the ratio of the nuclear quadrupole moments. Measured and assigned transitions and their hyperfine components of both isotopic species are listed in the supplementary material deposited in the AIP Physics Auxiliary Publication Service.[21]

Analysis of hyperfine structure

The spectrum and its hyperfine structure was analyzed with the computer program described previously[3] which determines simultaneously rotational and centrifugal distortion constants (I^r representation, A reduction[12]) as well as the quadrupole coupling constants of one or two nuclei by a nonlinear least-squares fit ("global fit") from observed frequencies of hyperfine components. The following coupling scheme was used:

$$\mathbf{J} + \mathbf{I_1} = \mathbf{F_1}, \quad |J - I_1| \leqslant F_1 \leqslant J + I_1,$$

$$\mathbf{F_1} + \mathbf{I_2} = \mathbf{F}, \quad |F_1 - I_2| \leqslant F \leqslant F_1 + I_2.$$

Because the relation between the Cartesian and spherical quadrupole coupling tensors and the final expression for the general matrix element of the quadrupole coupling operator $\hat{H}_{Q1} + \hat{H}_{Q2}$ derived earlier[3] contain typographical errors, the correct equations are given here, with F_3 as the component of F along the space-fixed e_3 axis (see also Ref. 13):

$$\langle F(F_1 I_2)F_3 F_1 (J I_1) I_2 K | \hat{H}_{Q1} + \hat{H}_{Q2} | \overline{F}(\overline{F}_1 I_2)\overline{F}_3 \overline{F}_1 (\overline{J} I_1) I_2 \overline{K} \rangle$$

$$= \delta_{F\overline{F}}\delta_{F_3\overline{F}_3}(-1)^K [(2J+1)(2\overline{J}+1)/24]^{1/2} \begin{pmatrix} J & 2 & \overline{J} \\ K & \overline{K}-K & -\overline{K} \end{pmatrix}$$

$$\times \left[\delta_{F_1\overline{F}_1}(-1)^{I_1+F_1} \begin{pmatrix} I_1 & 2 & I_1 \\ -I_1 & 0 & I_1 \end{pmatrix}^{-1} \begin{Bmatrix} F_1 & I_1 & J \\ 2 & \overline{J} & I_1 \end{Bmatrix} \chi_{1,\overline{K}-K}^{(2)} \right.$$

$$\left. + (-1)^{F+I_2-I_1-J-\overline{J}} [(2F_1+1)(2\overline{F}_1+1)]^{1/2} \begin{pmatrix} I_2 & 2 & I_2 \\ -I_2 & 0 & I_2 \end{pmatrix}^{-1} \begin{Bmatrix} I_1 & J & F_1 \\ 2 & \overline{F}_1 & \overline{J} \end{Bmatrix} \begin{Bmatrix} F & I_2 & F_1 \\ 2 & \overline{F}_1 & I_2 \end{Bmatrix} \chi_{2,\overline{K}-K}^{(2)} \right].$$

$$\chi_{J,0}^{(2)} = (3/2)^{1/2} \chi_{J,aa}.$$

$$\chi_{J,\pm 1}^{(2)} = \mp \chi_{J,ab} + i\chi_{J,ac},$$

$$\chi_{J,\pm 2}^{(2)} = (1/2)(\chi_{J,bb} - \chi_{J,cc}) \mp i\chi_{J,bc}.$$

Matrix elements due to $I_2 = 1(^{14}N)$ off-diagonal in F_1 were neglected. The program was modified to enable direct diagonalization of the whole F_1 block containing all matrix elements originating from $I_1 = 3/2$ (Br) for F_1 up to 59/2. This modification was essential for the successful analysis of the hyperfine splitting of the high J transitions.

All observed hyperfine components obeyed the approximate selection rules $\Delta F = \Delta F_1 = \Delta J$. The hyperfine structure due to the bromine quadrupole could be resolved completely into four components for all but a few transitions. The components $F = F_1 + 1$ and $F = F_1 - 1$ (due to ^{14}N) could never be resolved from each other. Both calculated frequencies were fit simultaneously to the same observed frequency. But they were usually resolvable from the component $F = F_1$.

Initial spectroscopic parameters were obtained as follows. The centrifugal distortion and the ^{14}N quadrupole coupling constants were transferred from the work on $CF_2{=}^{14}NCl$.[3] Rotational constants were calculated from an assumed structure (see the previous section). Estimates for the ^{79}Br quadrupole coupling constants were obtained by multiplying all constants reported for ^{35}Cl in $CF_2{=}NCl$[3] with -8.0 which is about the average of the ratios of the ^{79}Br and ^{35}Cl quadrupole coupling constants for similar molecules.

After the frequencies of the hyperfine components of the Q transitions had been measured precisely for $CF_2{=}^{14}N^{79}Br$, we analyzed these data in detail in order to gain as much information as possible before our search for the R transitions. The hyperfine structure of the transitions $J_{2,J-2}{-}J_{1,J-1}$ and $J_{1,J-1}{-}J_{0,J}$ followed approximately a first order perturbation pattern and could be fit without any problems by varying B, C, some centrifugal distortion constants, $\chi_{bb}^{Br} - \chi_{cc}^{Br}$ and $\chi_{bb}^{N} - \chi_{cc}^{N}$. However, the splitting pattern of the transitions $J_{3,J-3}{-}J_{2,J-2}$ exhibited some irregularities, particularly for the members $J = 21, 22, 23$ (Fig. 2). Upon inspection we discovered that the energy levels $J_{3,J-3}$ were rather close to the levels $J - 1_{4,J-5}$ (for $J = 21$, the separation was less than 2 GHz). The members of such a pair could interact with each other through a matrix element originating from χ_{ab} of the bromine atom. Exploratory calculations in which χ_{ab} was changed by ± 30 MHz indeed revealed that the splitting pattern depended critically on this parameter. However, changing χ_{ab} alone could not reproduce the observed pattern. Whenever two states are perturbed by an off-diagonal matrix element, the perturbation depends not only on the magnitude of that element but also on the energy difference between the interacting states. The only way to change this difference with given differences between rotational constants was to change all rotational constants simultaneously by the same amount. This had the effect of shifting the stacks of energy levels belonging to different J's with respect to each other. The splitting patterns in question were indeed very sensitive to such a change of rotational constants. Therefore, we tried to iterate simultaneous-
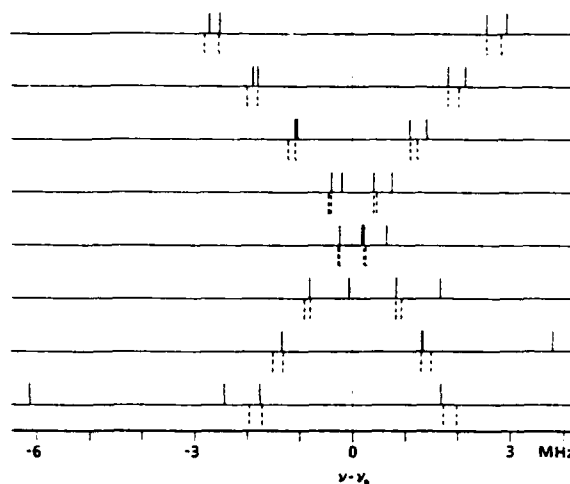
FIG. 2. $CF_2{=}^{14}N^{79}Br$. Hyperfine splitting patterns (corrected for ^{14}N splitting) for the transitions $J_{3,J-3}{-}J_{2,J-2}$, $J = 21$ (bottom) to $J = 28$ (top). ν_0: hypothetical unsplit frequency. Solid lines: observed and fit hyperfine components. Dashed lines: approximate "first-order" pattern calculated from the final constants by neglecting all matrix elements off-diagonal in J.

ly on all three rotational constants and all bromine quadrupole coupling constants and the least-squares fitting process converged. With the rotational constants obtained in this manner, the R transitions could be predicted accurately enough to identify them quickly (see the previous section). In the final stage of the analysis, over 300 frequencies of hyperfine components belonging to 32 transitions were fit to determine rotational and quartic centrifugal distortion constants as well as $\chi_{aa}^{Br}, \chi_{bb}^{Br} - \chi_{cc}^{Br}, \chi_{ab}^{Br}, \chi_{aa}^{N}$, and $\chi_{bb}^{N} - \chi_{cc}^{N}$ for both isotopic species.

The final constants are listed in Table I. Differences between observed and calculated frequencies are given in the supplementary material.[21] The quadrupole coupling tensors for the bromine atoms were transformed to their own principal axes system. The principal elements as well as the angle of rotation and the asymmetry parameter $\eta = (\chi_x - \chi_y)/\chi_z$ together with their standard errors are also listed in Table I. The parameter with the largest relative error and with the largest difference between the isotopic species was χ_{aa}^{N}. This is certainly due to the inability to resolve the hyperfine components $F = F_1 + 1$ and $F = F_1 - 1$ for any observed transition. There is no doubt that some low J transitions in a lower frequency region would experience resolvable separations between these components. All other parameters agreed well between the isotopic species and all but Δ_K could be determined with high accuracy.

Molecular structure

The inertial defects of 0.1916 and 0.1918 u Å^2 for $CF_2{=}^{14}N^{79}Br$ and $CF_2{=}^{14}N^{81}Br$, respectively, proved the planarity of the N–bromodifluoromethanimine molecule. The determination of a reliable molecular structure for this molecule by the diagnostic least-squares method[14,15] was hampered by the same difficulties as those encountered in the study of the N–chloro compound.[3] A different approach was chosen this time. The set of independent structural pa-

TABLE I. Rotational, centrifugal distortion, and quadrupole coupling constants of N–bromodifluoromethanimine.[a,b]

	$CF_2 = {}^{14}N^{79}Br$	$CF_2 = {}^{14}N^{81}Br$		$CF_2 = {}^{14}N^{79}Br$	$CF_2 = {}^{14}N^{81}Br$
A /MHz	11 252.312 6(17)	11 252.3042(20)	χ_{aa}^{Br}/MHz	584.34(26)	487.49(36)
B /MHz	1600.268 65(32)	1584.820 37(41)	$\frac{1}{4}(\chi_{bb}^{Br} - \chi_{cc}^{Br})$/MHz	90.128(10)	75.291(10)
C /MHz	1400.276 03(30)	1388.432 85(39)	χ_{ab}^{Br}/MHz	479.45(15)	400.44(13)
Δ_J/kHz	0.194 6(11)	0.1924(14)	χ_{bb}^{Br}/MHz	− 202.04(13)	− 168.45(18)
Δ_{JK}/kHz	2.185 7(72)	2.1388(78)	$\chi_{cc}^{Br} = \chi_{y}^{Br}$/MHz	− 382.30(13)	− 319.04(18)
Δ_K/kHz	9.16(33)	9.75(34)	χ_{x}^{Br}/MHz	− 428.91(14)	− 358.09(17)
δ_J/kHz	0.024 023(49)	0.023 415(44)	χ_z^{Br}/MHz	811.21(24)	677.13(34)
δ_K/kHz	1.413 5(75)	1.4006(78)	ϑ /deg[c]	25.323(8)	25.341(8)
χ_{aa}^{N}/MHz	2.39(25)	1.83(32)	η[d]	− 0.0575(2)	− 0.0577(1)
$\frac{1}{4}(\chi_{bb}^{N} - \chi_{cc}^{N})$/MHz	− 1.536 9(75)	− 1.5398(72)	σ/MHz[e]	0.0179	0.0172
χ_{ab}^{N} /MHz	− 2.73(13)	− 2.45(16)	n[f]	341	326
χ_{cc}^{N}/MHz	0.34(13)	0.62(16)			

[a] Standard errors in parentheses in units of last digit.
[b] χ_{bb}, χ_{cc} (for N, Br) and χ_x,χ_y,χ_z, ϑ and η (for Br) are dependent parameters.
[c] ϑ = angle between inertial principal axis a and quadrupole coupling tensor principal axis z (for Br).
[d] $\eta = (\chi_x - \chi_y)/\chi_z$ (for Br).
[e] Standard deviation.
[f] Number of fitted hyperfine components.

rameters contained the variables $r(NBr)$, $r(CN)$, $r(CF)$, $\alpha(BrNC)$, $\alpha(NCF_t)$, and $\alpha(FCF)$. The distances $r(CF)$ were required to be equal because the resulting difference $r(CF_t) - r(CF_c)$ depended heavily on the starting values of other parameters if this requirement was lifted. The angle $\alpha(FCF)$ instead of $\alpha(NCF_c)$ was included because a range of values for this angle in the $F_2C=$moiety has been reported in the literature. Only the rotational constants A and B of both isotopic species, weighted by the inverse square of their standard errors, were used to derive a plausible molecular structure. With this choice, three linear combinations of the six structural parameters became well determined. None of these contained significant contributions from the parameters $r(NBr)$ or $\alpha(FCF)$. Therefore, these parameters were kept constant during the fit. The value of 1.85 Å, chosen for $r(NBr)$, was transferred from the work on BrNCO[11] which was the only investigation reporting a NBr bond length in a Br–N=C moiety. The angle $\alpha(FCF)$ was kept constant at

one of the values 110°, 112°, or 114°. They covered the range of values for FCF angles reported in the literature for the $F_2C=$linkage (except[16] for $F_2C=O$, 107.9°). The value of 114.0° was chosen eventually because only in this case was the angle between the N–Br bond direction and the z principal axis of the bromine quadrupole coupling tensor smaller than 1°. Initial values and final results are listed in Table II. The estimated standard errors for the final values were obtained by using the diagnostic least-squares method with the estimated uncertainties 0.05, 0.02, and 0.01 Å for the distances $r(NBr)$, $r(CN)$ and $r(CF)$. respectively, and 2.0°, 1.0°, and 5.0° for the angles $\alpha(BrNC)$, $\alpha(NCF_t)$, and $\alpha(FCF)$, respectively.

For comparison, the molecular structure of N–chlorodifluoromethanimine was reevaluated by the same method. Except for the N–halogen distance. identical initial values were assumed. These results are also shown in Table II. together with the values reported earlier.[2,3] Apart from the N–

TABLE II Molecular structure of N–bromodifluoromethanimine and related molecules.[a,b]

Parameter	$CF_2 = NBr$		$CF_2 = NCl$				$CF_2 = NF$
	Initial	Final	Initial	Final	Ref. 3	Ref. 2	Ref 5
$r(NX)$	1.850	1.850(31)	1.700	1.700(31)	1.700	1.745	1.389
$r(CN)$	1.254	1.249(16)	1.254	1.246(16)	1.254	1.273	1.274
$r(CF_t) = r(CF_c)$	1.310	1.307(6)	1.310	1.307(6)	1.300	1.300	1.300
$\alpha(CNX)$	118.0	117.0(18)	118.0	116.4(18)	116.4	112.0	107.9
$\alpha(NCF_t)$	120.0	120.2(6)	120.0	120.3(6)	119.5	119.8	119.8
$\alpha(FCF)$	114.0	114.0(30)	114.0	114.0(31)	114.3	113.0	113.0
$\alpha(NCF_c)$[c]		125.8(25)		125.7(26)	126.2	127.2	127.2
ϑ[d]		25.8		27.1	27.15		

[a] Internuclear distances r in Å, bond angles α in degrees.
[b] Estimated standard errors in parentheses in units of last digit (see the text).
[c] Dependent parameter.
[d] Angle between "a" principal axis and NX bond direction

halogen distance and perhaps the angle α (halogen NC), the structures for the bromo- and chloro-compounds are about identical.

DISCUSSION

The experience and the information acquired during the investigation of the microwave spectrum of N–chlorodifluoromethanimine[3] proved to be very valuable for the successful assignment and analysis of the rotational spectrum of N–bromodifluoromethanimine reported here. The dominance of b-type transitions in the spectrum, approximate quadrupole coupling constants for ^{14}N and a reasonable estimate of the structure of these molecules could be derived from the data on $CF_2=NCl$. It was also possible to roughly estimate the diagonal and off-diagonal quadrupole coupling constants for bromine.

The most significant aspect of this investigation was the ability to determine the magnitude of all rotational constants from the hyperfine splitting patterns of Q transitions although usually only accurate differences between rotational constants can be obtained from Q transitions. These preliminary rotational constants were within 1.5 MHz of their final values. The prerequisites for this achievement were the presence of a large off-diagonal element of the quadrupole coupling tensor, the accessibility of sensitive transitions in the available spectral range and a crude estimate of the magnitude of the coupling element. A similar interaction has been used by Gerry and co-workers to determine accurate values for A and Δ_K in the near-prolate rotor spectrum of INCO from a-type transitions alone.[17]

The information from the $CF_2=NCl$ study and the rotational constants derived from Q transitions were important for this investigation because the rapid decomposition and the continuous flow system required a relatively large amount of sample. Nevertheless, we were able to record the spectrum, assign it and measure all reported frequencies precisely within a total of 15 nonconsecutive days on the spectrometer with about 4 mmol of sample.

The supplementary material[21] contains a number of cases in which two frequencies were reported with a separation of as low as 0.12 MHz. Of course, two lines with bandwidth at half-height of just less than 0.2 MHz were not baseline resolved in such a case. However, in all these instances, the weaker component of such a doublet split by the ^{14}N hyperfine interaction was observed as a distinct step in the recording of the signal and not just a fuzzy shoulder.

The standard deviations of the least-squares fits for both isotopic species are less than 0.018 MHz. Nevertheless, the residuals of the $|F - F_1| = 1$ components of the lower J transitions exhibit a systematic trend which was caused by the fact that these unresolvable components were always fitted to the same observed frequency. A better way to account for the unresolvable components would have been to fit the average of the calculated frequencies, weighted by intensities, to the observed frequency. This procedure would reduce the number of data points and would remove the systematic part of the residuals. The effort to program such a procedure including the calculation of relative intensities did not seem necessary nor worthwhile because the standard deviations were already as low as the experimental precision of the data.

The ratios between corresponding quadrupole coupling constants for the bromine isotopes were between 1.1971 and 1.1994, with an average of 1.1981, which is within 0.001 of the ratio of the nuclear quadrupole moments.[18] This was also true for elements of the quadrupole coupling tensors expressed in the principal inertial axes system, indicating that the principal inertial axes have essentially the same orientation with respect to the molecular frame. An ionic character of 4.6% for the N–Br bond with the net positive charge on the bromine atom was derived from the bromine quadrupole coupling constants according to the Townes and Daily model.[18] Similarly, the π character of this bond was estimated to be 4.0% from the asymmetry of the diagonalized quadrupole coupling tensor.

Whereas this investigation yielded quite accurate spectroscopic data about N–bromodifluoromethanimine, the structural information derived from them were less satisfactory. Although we were able to propose structures for both $CF_2=NBr$ and $CF_2=NCl$ consistent with each other, a number of problems remained. The bond length $r(NBr)$ was of greatest interest but nothing new could be learned about it. The angle α (CNBr) was definitely larger than the corresponding angle α (CNF) in $CF_2=NF$.[5] However, the question as to how much larger could not be answered finally. The only structural parameter almost independent from assumptions and initial values was the angle $\alpha(NCF_1)$ of about 120°. All other parameters depended to a large extent on the initial assumptions. Without the information from the quadrupole coupling tensor (angle between a and z axis), it would have been even harder to decide between different possible solutions. If we assume that the z axis is more or less aligned with the direction of the straight line connecting the N and Br nuclei, this angle required a bond length $r(CN)$ much shorter than the r_s values determined for $CH_2=NH$[19] and $CH_2=NOH$[20] of approximately 1.275 Å, and an angle α (FCF) much larger than the r_0 value of 107.9° reported for $CF_2=O$.[16] The r_α^0 structure of $CF_2=NF$ derived from microwave and electron diffraction data[5] is definitely different from the structures of $CF_2=NBr$ and $CF_2=NCl$. The differences in the quadrupole coupling constants χ_{cc} for ^{14}N in these molecules are an indication for different electronic environments which very well may translate into different molecular structures. The electronic and structural differences between the $CF_2=NX$ molecules depend, of course, on the relative electronegativities of the halogen atoms with respect to nitrogen. Nevertheless, only data from additional isotopic modifications (^{15}N, ^{13}C) will be able to resolve the questions about the exact geometry of the $C=N-X$ moiety in these halogenated imines.

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Molecular Structure and Internal Rotation Potential of Perfluoro-2,3-diaza-1,3-butadiene, $CF_2=N—N=CF_2$. An Electron Diffraction and ab Initio Study

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A gas-phase electron diffraction study of perfluoro-2,3-diaza-1,3-butadiene results in a planar trans structure with the following geometric parameters (r_a values with 3σ uncertainties): N—N = 1.421 (12), C=N = 1.264 (7), C—F = 1.304 (4) Å; N—N=C = 112.7 (9), F—C—F = 110.8 (9)°. The CF_2 groups are tilted by 5.0 (8)° toward the nitrogen lone pairs. No additional conformer has been observed. Ab initio calculations for $CH_2=N—N=CH_2$ (6-31G** basis) and $CF_2=N—N=CF_2$ (6-31G* basis) demonstrate that the internal rotation potentials change drastically if electron correlation is included at the MP2 level. Whereas SCF–HF calculations predict the planar trans forms to be the only stable conformers, the MP2 method predicts additional high-energy gauche conformers with $\Delta E \approx 0.8$ ($CH_2=N—N=CH_2$) and 1.8 kcal mol^{-1} ($CF_2=N—N=CF_2$). Both values are in good agreement with experiment, $\Delta E = 1.2$ (5) kcal mol^{-1} for the parent compound and $\Delta G \geq 1.8$ kcal mol^{-1} for the fluorinated species.

Introduction

Structure and conformational properties of the simplest conjugated systems, 1,3-butadiene and the isoelectronic glyoxal, have attracted considerable interest over the past decades. It is well established by experimental methods (electron diffraction,[1] vibrational spectroscopy[2]) and by ab initio calculations[3,4] that the

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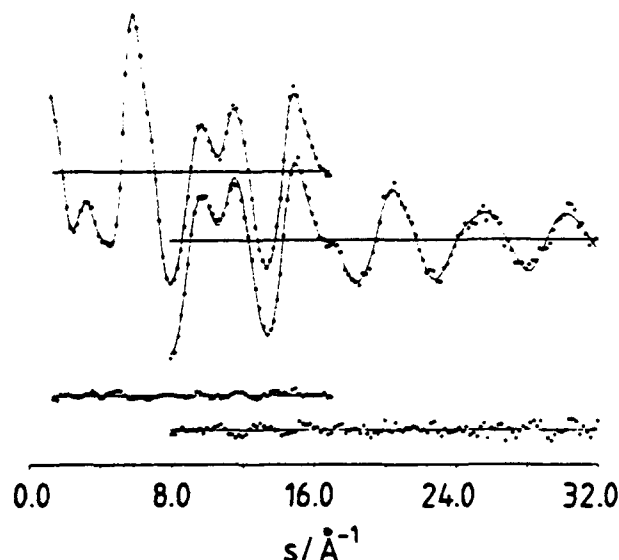
Figure 1. Experimental (●●●) and calculated (—) molecular intensities and differences.

Figure 2. Experimental radial distribution function and difference curve.

most stable conformer of 1,3-butadiene is the planar trans form and the less stable conformer has a cis-gauche structure. From calorimetric[5] and spectroscopic data[2,6] an energy difference between 2.1 and 3.1 kcal mol⁻¹ is estimated in good agreement with high-quality ab initio calculations,[3] which predict 3.15 kcal mol⁻¹. Glyoxal experimental studies (electronic[7,8] and microwave spectra[9]) and ab initio calculations[10] find a high-energy planar cis conformer beside the most stable planar trans structure.[11] For this compound experimental values for the energy difference of 3.2 (6) and 3.8 (6) kcal mol⁻¹ have been reported,[7,12] and ab initio calculations predict values of 5.86,[11a] 5.6,[11b] 5.1,[11c] and 4.25 kcal mol⁻¹.[11d] An electron diffraction study[13] for the isoelectronic 2,3-diaza-1,3-butadiene (formaldazine), CH₂=N—N=CH₂, which was carried out at temperatures between −30 and +225 °C, results in a mixture of trans and cis-gauche conformers with an energy difference of 1.2 (5) kcal mol⁻¹. The existence of a second high-energy conformer is confirmed by matrix IR spectra.[14]

Fluorination has a drastic effect on the conformation of 1,3-butadiene. Gas-phase electron diffraction[15] and photoelectron and optical spectra[16] demonstrate that in perfluoro-1,3-butadiene the cis-gauche conformation is the most stable structure and no

Table I. Results of Electron Diffraction Analysis for CF₂=N—N=CF₂

(a) Geometric Parameters[a]			
C=N	1.264 (7)	F—C—F	110.8 (9)
C—F	1.304 (4)	tilt[b]	5.0 (8)
N—N	1.421 (12)	(CNNC)_eff	153 (5)
N—N=C	112.7 (9)		

(b) Interatomic Distances and Vibrational Amplitudes				
C=N	1.26	0.040[c]	C—C′	3.30	0.070[c]
C—F	1.30	0.046 (6)	N—F₁′	3.47	0.084 (16)
N—N	1.42	0.050[c]	C—F_c′	3.84	0.16 (5)
F_c—F₁	2.15	0.056 (10)	C—F₁′	4.41	0.09 (3)
N—C′	2.24		F_c—F_c′	4.67	0.15 (3)
N—F₁	2.22		F_c—F₁′	4.70	
N—F_c	2.32	0.073 (9)	F₁—F₁′	5.61	0.11 (5)
N—F_c′	2.66				

(c) Agreement Factors for the Two Camera Distances[d]
$$R_{50} = 0.039 \qquad R_{25} = 0.134$$

[a] r_a values in angstroms and degrees. Estimated uncertainties are 3σ values and include systematic errors (see text). [b] Tilt angle of CF₂ group toward nitrogen lone pair. [c] Not refined. [d] $R = [\sum w_i \Delta_i^2 / \sum w_i (s_i M_i^{exp})^2]^{1/2}$; $\Delta_i = s_i M_i^{exp} - s_i M_i^{calc}$; w_i = weight.

contribution of the planar trans conformer has been observed. This experimental observation has recently been reproduced correctly by ab initio calculations that predict the planar trans conformation to be higher in energy by 1.8 kcal mol⁻¹ relative to the gauche structure.[17] IR and Raman spectra[18] and electron diffraction intensities[19] for oxalyl fluoride, (COF)₂, are interpreted as a mixture of planar trans and cis conformers in the gas phase, with the trans form favored but indicating that the energy difference between these two conformations is lowered appreciably upon fluorination. This has been confirmed by ab initio calculations that predict the cis form to be higher in energy by only 0.54 kcal mol⁻¹ (4-31G basis) or 0.13 kcal mol⁻¹ (STO-4G basis) than the trans conformer.[20]

The first synthesis of the perfluorinated species of 2,3-diaza-1,3-butadiene has been reported by Mitsch.[21] The IR (gas) and Raman (liquid) spectra were interpreted in terms of a planar trans configuration.[22] In this study we report a structure determination of CF₂=N—N=CF₂ by gas electron diffraction with special attention to the possible presence of a second conformer. For further elucidation of the effect of fluorination on the shape of the internal rotation potential, we perform ab initio calculations for CH₂=N—N=CH₂ and its perfluorinated species.

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Table II. HF-Optimized Geometries (Å, deg) for $H_2C=N-N=CH_2$ at Various CNNC Dihedral Angles (deg) and Relative HF Energies (ΔE_{HF}^{HF}) and MP2 Energies (kcal mol^{-1}) at HF Geometries (ΔE_{HF}^{MP}) and MP2 Geometries (ΔE_{MP}^{MP})

CNNC	N—N	N=C	C—H$_t$	C—H$_c$	NNC	HCH	tilt[a]	ΔE_{HF}^{HF} [b]	ΔE_{HF}^{MP} [c]	ΔE_{MP}^{MP} [d]
cis	1.411	1.251	1.077	1.081	122.3	116.7	4.7	16.61	14.87	14.70
30	1.386	1.253	1.076	1.082	120.5	117.8	3.5	11.23		
60	1.369	1.252	1.076	1.082	118.3	118.8	2.5	5.18	1.92	2.03
75	1.368	1.251	1.076	1.082	117.8	118.7	2.4	4.02	0.89	1.06
90	1.370	1.250	1.076	1.082	117.3	118.7	2.4	3.54	0.65	0.86
105	1.375	1.250	1.076	1.081	116.3	118.7	2.4	3.20	0.72	
120	1.383	1.250	1.076	1.081	115.0	118.8	2.4	2.64	0.74	0.90
150	1.392	1.252	1.076	1.080	113.0	119.0	2.2	0.90		
trans	1.396	1.253	1.076	1.080	112.3	119.2	2.1	0.00	0.00	0.00

[a]Tilt angle of CH$_2$ group toward nitrogen lone pair. [b]$E_t = -186.892\,867\,4$ au. [c]$E_t = -187.485\,011\,5$ au. [d]$E_t = -187.488\,506\,8$ au; all E_t values at the trans configuration.

Experimental Section

CF$_2$=N—N=CF$_2$ was prepared by the low-pressure pyrolysis of CF$_2$=N—Br at 550 °C.[23] The IR spectra at 10 and 100 Torr indicated no impurities.

The electron diffraction intensities were recorded with the Balzers KD-G2 gas diffractograph[24] at two camera distances (25 and 50 cm). The electron wavelength (ca. 60 kV accelerating voltage) was calibrated with ZnO diffraction patterns. The sample reservoir was kept at –53 °C, and the stainless steel inlet system and nozzle were at room temperature. The camera pressure never exceeded 10^{-5} Torr during the experiment. Due to the very small amount of sample available, only two photographic plates (Kodak Electron Image plates, 13 × 18 cm) could be exposed at each camera distance. Both short-distance plates were rather light (optical densities below 0.1), which makes the intensities for this s range more noisy than usual. The four plates were evaluated by the usual procedures,[25] and the averaged molecular intensities in the s ranges 1.4–17 and 8–32 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} are presented in Figure 1.

Structure Analysis for CF$_2$=N—N=CF$_2$. The radial distribution curve (Figure 2) was calculated with an artificial damping constant of 0.002 Å^2. The geometric structure of the planar trans configuration is characterized by three bond lengths (N—N, N=C, C—F), two bond angles (NNC, FCF), and a tilt angle between the FCF bisector and the N=C bond direction (tilt in the molecular plane; positive values imply tilt toward nitrogen lone pair). Preliminary structure refinements indicated that an effective dihedral angle[26] (CNNC)$_{eff}$ < 180° had to be introduced as an additional parameter in order to account for the large amplitude torsional vibration around the N—N bond. The vibrational amplitudes for the N—N and N=C distances had to be constrained in the least-squares analyses. Further assumptions for the vibrational amplitudes are evident from Table I. With these constraints seven geometric parameters and nine vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.6|: NC/CF = –0.94, CF/FCF = –0.61, NNC/tilt = –0.64, CF/1(CF) = –0.86, and NC/1(CF) = 0.89. The molecular intensities were modified with a diagonal weight function,[25] and scattering amplitudes and phases of Haase[27] were used in the least-squares analyses. The final results are summarized in Table I. Estimated uncertainties are based on 3σ values and include possible systematic errors due to the assumptions made for bonded vibrational amplitudes. These contributions were estimated by varying the values for the N—N and N=C amplitudes by ±0.005 Å.

Model calculations demonstrate that the molecular intensities at small scattering angles and the radial distribution curve in the region of long nonbonded distances are very sensitive toward small contributions from a cis-gauche conformer. Such a structure is characterized by several nonbonded C—F and F—F distances around 4 Å, where no distances in the trans conformer occur, and by no distances in the region 4.2 < r < 5 Å, where several distances in the trans conformer occur. A series of least-squares analyses with various but fixed contributions of the gauche conformer were performed. The bond lengths and angles for the gauche conformer were constrained to the values for the trans form, except for the NNC angle, which was increased according to the ab initio calculations (see below). The CNNC dihedral angle was varied from 60 to 100°. The agreement factor for the long camera distance data, R_{50}, increased in all these analyses, and we estimate an upper limit of 10%

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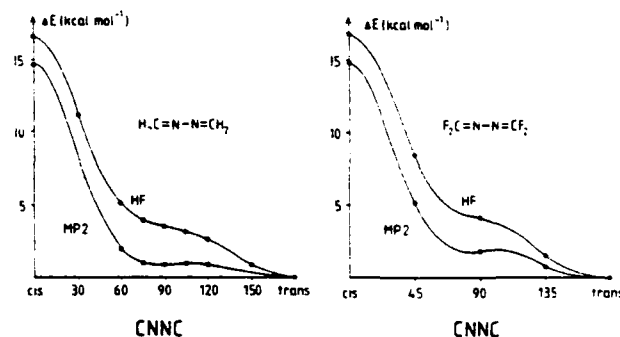
Figure 3. Calculated internal rotation potentials at HF and MP2 approximations.

gauche contribution, which leads to an increase of R_{50} by 20%. This corresponds to a lower limit of 1.8 kcal mol^{-1} for the free enthalpy difference between gauche and trans conformers.

Ab Initio Calculations

The shapes of the potentials for internal rotation in 1,3-butadiene[4] and glyoxal[10] have been studied repeatedly in great detail by ab initio methods. Less sophisticated calculations in the HF approximation using split valence basis sets without polarization functions have been reported for the isoelectronic 2,3-diaza-1,3-butadiene.[28] If the experimental geometries are used, a potential with a single minimum at the trans position is predicted. The experimental findings, i.e. a second higher energy gauche conformer, are reproduced qualitatively with partial adjustment of the geometry. This gauche conformation at CNNC ~ 80° lies 3.5 kcal mol^{-1} above the trans structure. Since we were interested in the effect of fluorination on the internal rotation potential, we performed calculations for the parent diaza compound and for the perfluorinated species. The program suite GAUSSIAN 82[29] and double-ζ basis sets with polarization functions (6-31G**) were used.

2,3-Diaza-1,3-butadiene. Geometries were fully optimized by HF gradient methods for various CNNC dihedral angles between 0 (cis) and 180° (trans) in steps of 30°. Two additional points at 75 and 105° were included. The geometric parameters and relative HF energies (ΔE_{HF}^{HF}) are summarized in Table II. Deviations of the CH$_2$ groups from coplanarity with the NNC plane are minor and are not given in the table. The torsional potential is displayed in Figure 3 (curve HF). At the HF level the potential for internal rotation has a shoulder around the 90° dihedral angle and 3.5 kcal mol^{-1} above the trans conformation but no second minimum. This is in direct conflict with the experiments,[13,14] and therefore, further calculations that go beyond the HF level were performed. The relative energies obtained in second-order Moller–Plesset approximation (MP2)[30] for the HF-optimized geometries (ΔE_{HF}^{MP}) are also listed in Table II. This internal rotation potential (not displayed in Figure 3) has a very flat second minimum at a dihedral angle near 90°, about 0.6 kcal mol^{-1} above the trans structure.

Since HF calculations with 6-31G** basis sets are known to result in too short bond lengths, which may have a small but in our case significant influence on the internal rotation potential, we estimated this effect by optimizing the skeletal parameters (N—N, N=C, NNC) for the trans configuration at the MP2 level. Inclusion of electron correlation lengthens the N—N and N=C bonds by about 0.03 and 0.04 Å and

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Table III. HF-Optimized Geometries (Å, deg) for $F_2C=N-N=CF_2$ at Various CNNC Dihedral Angles (deg) and Relative HF Energies (ΔE_{HF}^{HF}) and MP2 Energies (kcal mol^{-1}) at MP2-Adjusted Geometries (ΔE_{MP}^{MP})

CNNR	N—N	N=C	C—F$_t$	C—F$_c$	NNC	FCF	tilt[a]	ΔE_{HF}^{HF}[b]	ΔE_{MP}^{MP}[c]
cis	1.376	1.231	1.290	1.293	128.8	108.9	5.4	16.71	14.74
45	1.378	1.231	1.287	1.296	121.6	110.1	3.1	8.46	5.26
90	1.384	1.230	1.287	1.294	117.1	110.4	2.5	4.17	1.86
135	1.386	1.233	1.288	1.290	114.6	110.4	3.0	1.55	0.81
trans	1.387	1.235	1.288	1.287	113.3	110.4	3.3	0.00	0.00

[a] Tilt angle of CF$_2$ groups toward nitrogen lone pair. [b] Total energy $E_t = -582.3146042$ au. [c] $E_t = -583.5542907$ au; both values at the trans configuration.

Table IV. Experimental and Calculated Geometric Parameters (Å, deg) for the Trans Configurations of $H_2C=N-N=CH_2$ and $F_2C=N-N=CF_2$

	$H_2C=N-N=CH_2$			$F_2C=N-N=CF_2$	
	expt[a]	HF	MP2[b]	expt[c]	HF
N—N	1.418 (3)	1.396	1.432	1.421 (12)	1.387
N=C	1.277 (2)	1.253	1.285	1.264 (7)	1.235
NNC	111.4 (2)	112.3	109.8	112.7 (9)	113.3
C—X$_t$	1.094 (5)	1.076	1.076	1.304 (4)	1.288
C—X$_c$		1.080	1.080		1.287
XCX	118.6 (12)	119.2	119.2	110.8 (9)	110.4
tilt[d]	0.0[e]	2.1	2.1	5.0 (8)	3.3

[a] r_s values from ref 13 for -30 °C nozzle temperature. [b] Only the skeletal parameters (N—N, N=C, NNC) were optimized at the MP2 level; the CH$_2$ parameters correspond to HF level. [c] r_a values from this study. [d] Tilt of CX$_2$ groups toward nitrogen lone pair. [e] Not refined.

decreases the NNC angle by 2.5° (the values are given in Table IV). For all other dihedral angles the HF values were adjusted accordingly. Since previous calculations for methanimine, $HN=CH_2$,[31] had demonstrated that electron correlation has minor effects on the geometry of the CH$_2$ group, we felt justified to keep these parameters at the HF level. The relative MP2 energies obtained for these "MP2-optimized" geometries (ΔE_{MP}^{MP}) are also included in Table II, and the potential function is displayed in Figure 3 (curve MP2). This potential function is very similar to the MP2 values based on HF geometries. It has a shallow minimum around the 85° dihedral angle, about 0.8 kcal mol^{-1} above the trans configuration. The influence of the geometric parameters (HF- or MP2-optimized) used on the MP2 calculations is small, and we consider the ΔE_{MP}^{MP} values as the best theoretical data available at that time.

Perfluoro-2,3-diaza-1,3-butadiene. Computer-time constraints dictated a rather coarse grid for the dihedral angles in this compound and obviously did not allow geometry optimizations at the MP2 level. The HF-optimized geometries (6-31G* basis set) in steps of 45° and the relative energies (ΔE_{HF}^{HF}) are summarized in Table III, and the torsional potential is displayed in Figure 3. Out of plane distortions for the CF$_2$ groups are again small and not listed in the table. For the MP2 calculations the geometric parameters for the C=N—N=C skeleton were adjusted by transfering the corresponding differences for the trans conformer of the parent compound (see Table IV) to the HF values of the fluorinated species. This procedure appears to be justified on the basis of previous calculations for $HN=CH_2$ and $HN=CF_2$, where the effect of electron correlation on the N=C bond length was shown to be nearly independent of fluorination (0.032 and 0.028 Å, respectively).[31] The effect of electron correlation on the C—F bond lengths was transfered from $HN=CF_2$.[31] This may not be a perfectly correct estimate of the geometric effects of electron correlation, but the above calculations for $CH_2=N-N=CH_2$ had demonstrated that the internal rotation potential depends only very moderately on the geometry (HF- or MP2-optimized). The ΔE_{MP}^{MP} values (Table III and Figure 3) demonstrate a strong effect of electron correlation on the torsional potential. The coarse grid of points calculated along the internal rotation coordinate and the level of theory (estimated geometries and MP2 approximation), however, do not allow the prediction of quantitative results. The similarity of this potential function with that for $CH_2=N-N=CH_2$ suggests the existence of a second minimum around the 90° dihedral angle and about 1.8 kcal mol^{-1} above the planar trans conformation.

Results and Discussion

The conformational properties of the C=N—N=C skeleton do not change qualitatively with fluorination. In the parent and fluorinated compounds the planar trans structure is predominant

and higher energy conformers are observed ($CH_2=N-N=CH_2$) or predicted ($CF_2=N-N=CF_2$). In the perbrominated derivative, however, only the trans-gauche structure with CNNC = 107.9 (5.2)° is observed in an electron diffraction analysis.[32]

The experimental and calculated geometric parameters of 2,3-diaza-1,3-butadiene and the fluorinated species are collected in Table IV. It is well-known that bond lengths at the HF level with 6-31G* basis sets are shorter than experimental values by about 0.02–0.03 Å, and MP2 values are longer by about 0.01–0.02 Å. HF values for bond angles agree with experimental values to within 1–2°.

Fluorination has only minor effects on the skeletal geometries. The calculations predict slight shortening of the N—N bond, but this difference is smaller than the experimental uncertainties. Comparison of the N—N bond lengths in the diaza compounds with those in hydrazines (1.449 (2) Å in H_2N-NH_2,[33] 1.417 (6) Å in $(CH_3)_2N-NH_2$,[34] 1.410 (4) Å in $(CH_3)_2N-N(CH_3)_2$[35]) indicates very little or no conjugation in the C=N—N=C skeleton. This is also supported by the ab initio calculations, where (p–p)π overlap populations perpendicular to the molecular plane of 0.008 au in $H_2C=N-N=CH_2$ and -0.020 au in $F_2C=N-N=CF_2$ are predicted. The N=C bonds shorten upon fluorination (0.013 (8) Å from experiment and 0.018 Å from calculations), and this observation is in agreement with an earlier study of the effect of fluorination in methanimine.[31] The NNC angles increase marginally with fluorination. The effective dihedral angle in $CF_2=N-N=CF_2$ (153 (5)°; see Table I) due to the large amplitude torsional vibration around the N—N bond is very similar to the corresponding values for $CH_2=N-N=CH_2$ (160 (5) at 60 °C)[13] and $CH_2=C-C=CH_2$ (157 (2)° at 25 °C).[1]

It is generally assumed[36] that electron correlation has a negligible effect on single-bond rotational potentials, and this has been demonstrated explicitly for 1,3-butadiene[3] and glyoxal.[10a] This, however, is not true for 2,3-diaza-1,3-butadiene, where electron correlation changes the shape of the potential function qualitatively (Figure 3) by introducing an additional minimum and lowers the relative energy at the gauche position by about 3 kcal mol^{-1}. This gauche minimum occurs at an angle slightly larger ($\sim$85°) than that obtained from the electron diffraction experiment (62 (20)°), and the energy differences are in good agreement with each other ($\Delta E_{MP}^{MP} = 0.8$, $\Delta E^{exp} = 1.2$ (5) kcal mol^{-1}).[13] Electron correlation has a very similar effect on the internal rotation potential of the perfluorinated species, resulting in a shallow gauche minimum about 1.8 kcal mol^{-1} above the trans conformation. This is in reasonable agreement with the experimental estimate of $\Delta G \geq$ 1.8 kcal mol^{-1}.

Beside this unexpectedly large effect of electron correlation, the internal rotation potentials in the diaza compounds differ also in other aspects from such potentials in the isoelectronic analogues. Whereas the potential curves of 1,3-butadiene and glyoxal have their maxima around 105 and 75°, respectively, and a low barrier

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(1,3-butadiene) or a minimum (glyoxal) at the cis position, the potential functions for the diaza compounds have their maxima at the cis position. The barriers to internal rotation around the N—N bond are predicted to be much higher (ΔE_{MP}^{MP} = 14.5 and 14.7 kcal mol^{-1}, respectively) than those around C—C bonds (ΔE_{HF}^{HF} = 6.07[3] and 5.7[17] kcal mol^{-1} in 1,3-butadiene and its perfluorinated species or 6.80[10a] and 5.23[20] kcal mol^{-1} in glyoxal or oxalyl fluoride). Further distinct differences between 1,3-butadiene and glyoxal on one hand and 2,3-diaza-1,3-butadiene on the other hand, are the geometry changes occuring during internal rotation. The C—C bond lengths have their minimum values at the trans configuration, their maximum values near the barrier, and intermediate values at the cis position.[3,10c] (The variations of the C—C bond lengths in glyoxal reported in ref 10a differ from those reported in ref 10c.) On the other hand, the N—N bond in CH_2=N—N=CH_2 *shortens* in going from trans to gauche by about 0.028 Å and increases to a maximum value at the cis position. In CF_2=N—N=CF_2 the N—N bond has its maximum length at the trans configuration and shortens monotonically in going to cis. A strong difference between the =C—C= and =N—N= skeletons is also evident from the variations in the bond angles upon internal rotation: whereas the C—C=C and C—C=O bond angles increase only slightly by 3.2 and 1.6° between trans and cis configuration, the N—N=C angles increase by 10.0 and 15.5° in the parent and fluorinated species. This strong angle distortion can be considered as a consequence of the much smaller value for the "unstrained" N—N=C angle in the trans position (112.3°) relative to the corresponding values for C—C=C (124.0°) or C—C=O (121.1°).

Fluoride-Promoted Competitive Reactions of Cyanogen Fluoride, Perfluoromethanimine, and Pentafluoro-2-azapropene[1]

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Abstract: Competitive reactions of cyanogen fluoride ($FC \equiv N$), perfluoromethanimine ($CF_2 = NF$), and pentafluoro-2-azapropene ($CF_3N = CF_2$) were performed by combining pairs of the substrates over KF or CsF. These reactions establish the order of reactivity with fluoride ion as $CF_2 = NF > CF_3N = CF_2 \gg F - C \equiv N$. Subsequent reactions of the addition products with fluoride ion, ClF, and Br_2/CsF are discussed. Seven new compounds, including a novel diaziridine, were characterized by IR, NMR, MS, and physical properties.

Fluoride-promoted reactions of fluorinated nitriles and imines have produced a number of interesting classes of compounds.[2-5] Implicit to the mechanism of these reactions is the presence of an intermediate nitrogen-based anion that can be easily oxidized by halogens and can serve as a reactive nucleophile in some cases. Perfluoromethanimine, $CF_2 = NF$, readily forms a nucleophilic anion, CF_3NF^-, in the presence of KF or CsF.[4] Different dimers of $CF_2 = NF$ are formed, $CF_3NFCF = NF$ or

$$CF_3N - CF_2$$
$$\diagdown N \diagup$$
$$F$$
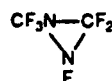
depending on the choice of alkali metal fluoride catalyst. The anion, CF_3NF^-, can also be oxidized by bromine to CF_3NBrF.[6] On the other hand, trifluoroacetonitrile is much less reactive with fluoride ion. The resultant anion, $CF_3CF = N^-$, is unreactive in a nucleophilic sense but is easily oxidized by bromine to the corresponding N-bromimine.[7] In order to study the competitive reactivity of some simple fluorinated nitrogen anions, we have chosen FCN, $CF_2 = NF$, and $CF_3N = CF_2$ as substrates for alkali metal fluoride promoted reactions.

Although cyanogen fluoride has been known for over 50 years, its reaction chemistry has been limited by its availability and its explosive behavior, especially in the liquid phase.[8] Schachner and Sundermeyer have reported some reactions of FCN with CsF as a catalyst.[5] Scheme I summarizes the previous work on FCN.

Perfluoromethanimine was studied extensively by Chang and DesMarteau.[4,6] The intermediacy of a nucleophilic anion, CF_3NF^-, has been inferred in KF- and CsF-promoted reactions of $CF_2 = NF$.[4] The facile dimerization and other reactions of pentafluoro-2-azapropene, $CF_3N = CF_2$, with KF and CsF substantiate intermediacy of the reactive anion, $(CF_3)_2N^-$.[3,9] However, none of the studies have provided a basis for determining the relative reactivities of these substrates with fluoride ion. Furthermore, no estimation of the relative nucleophilicities of these reactive anions has been obtained.

In this work, a relative order of reactivity of these substrates with fluoride ion is established by competitive reactions. In addition, the order of nucleophilicity of the respective nitrogen anions can be determined from the relative product distribution. The

Scheme I

cat	cat	prod.
COF_2	CsF	$CF_3N = C = O$
SF_4	CsF	$CF_3N = SF_2$
SOF_4	CsF	$CF_3N = S(O)F_2$
2HF	—	CF_3NH_2
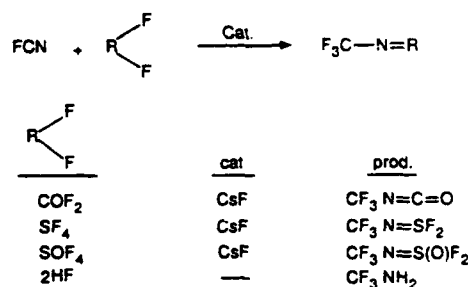
competitive reactions produce two perfluorinated N-cyano compounds, CF_3NFCN and $(CF_3)_2NCN$, a substituted imine adduct, $CF_3NFCF = NCF_3$, and a symmetrical N,N'-bis(trifluoromethyl)diaziridine

$$CF_3N - NCF_3$$
$$\diagdown \diagup$$
$$CF_2$$
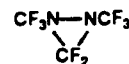
Some derivatization of the N-cyano compounds to N,N-dichloramines, $(CF_3)_2NCF_2NCl_2$ and $CF_3NFCF_2NCl_2$, N-bromimine, $(CF_3)_2NCF = NBr$, and an N,N-difluoramine, $(CF_3)_2N-CF_2NF_2$, was accomplished by reactions with ClF, Br_2/CsF, and F_2/CsF.

Experimental Section

General Methods. All volatile materials were handled in either a stainless steel (Type 304 or 316) or a glass vacuum system equipped with stainless steel or Teflon–glass valves, respectively. Pressures were measured with a Wallace and Tiernan Series 1500 differential pressure gauge. Amounts of reactants and products were measured by PVT measurements, assuming ideal gas behavior. Temperatures were measured by a digital readout iron–constantan thermocouple.

Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrometer with a Model 7500 data station, with a 10-cm glass cell fitted with KCl windows. [19]F spectra were recorded either on a JEOL FX-90Q or on an IBM NR200AF with CFCl$_3$ as the reference and CDCl$_3$, acetone-d_6, or benzene-d_6 as the lock solvent. Mass spectra were recorded on a Hewlett-Packard 5985-B spectrometer at 70 eV for EI and CI (CH$_4$). Samples were introduced by direct gas injection.

Reagents. FCN was prepared by a modification of the literature technique.[8] Cyanuric fluoride (made from cyanuric chloride by the method of Tullock and Coffman[10]) was contained in a Pyrex vessel fitted with two Teflon–glass valves and containing 1 g of NaF at 0 °C. A stream of nitrogen was passed through a flow system consisting in sequence of a CaSO$_4$ drying column, a mass flowmeter, a trimer vessel, a 3 ft × $^3/_8$ in. o.d. platinum tube heated in an electric furnace to 1100 °C, and a Pyrex trap cooled to −196 °C in a hood. The flow rate was maintained at 200–500 cm^3 min for 1–2 h in a typical run, and 2–5 g of (FCN)$_3$ was consumed. The products were separated by fractionation

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through a series of cold traps under dynamic vacuum. A -110 °C trap retained unreacted cyanuric fluoride and cyanogen. A -125 °C trap retained FCN, and a -196 °C trap collected CF_3CN and $CF_3N=CF_2$. Repeated distillation was necessary to obtain pure FCN. Yields of FCN were typically 20% while CF_3CN and $(CN)_2$ comprised 20-30% of the products. The balance was unreacted cyanuric fluoride and small amounts of other unidentified products.

Caution: Cyanogen fluoride has been shown to polymerize explosively and must be handled with extreme caution. We have not experienced any explosive behavior while handling 3-30-mmol samples in glass vacuum systems at FCN pressures of less than 1 atm.

Fluorine was obtained from Air Products and Chemicals, Inc., and was passed through a NaF scrubber before use. ClF was made by combining equimolar amounts of Cl_2 and F_2 (0.1 mol) in a Monel cylinder (150 mL) and heating the cylinder at 230 °C for 18 h. (*Caution*: This reaction proceeds via a contained explosion, occurring at ~120 °C.) Pure ClF was removed as a gas from the cylinder at -111 °C.

$CF_2=NF$ and $CF_3N=CF_2$ were synthesized by literature methods.[11,12] KF and CsF were activated by fusion in a platinum crucible and grinding in a ball mill under very anhydrous conditions. Other reagents were used as received or were purified by standard procedures. As necessary, product samples were further purified by GLC with a 10-ft column packed with 15-30% halocarbon oil on Chromasorb-P.

General Procedure for Competitive Reactions. All competitive reactions involving pairs of the imines or nitriles were carried out in two-piece 100-mL Pyrex reactors fitted with a Teflon–glass valve, joined by Ace-Thred connectors with Viton O-rings, and containing a magnetic stirring bar. In a typical reaction, 1 g of KF (~17 mmol) was added to the reactor in a drybox. The reactor was evacuated and cooled to -196 °C before the two reactants were introduced in equimolar amounts (1-3 mmol each) by vacuum transfer. After the mixture warmed from -196 to +22 °C, it was allowed to stir for 12 h before the volatiles were removed and separated by trap-to-trap distillation and further purified by GLC as needed.

Preparation and Characterization of the Competitive Reaction Products. $(CF_3)_2NC=N$. On a 3-mmol scale for FCN and $CF_3N=CF_2$ with 17 mmol of KF as a catalyst, $(CF_3)_2NCN$ was obtained in 70% yield. The remainder of the product was the dimer of the azapropene, $(CF_3)_2NCF=NCF_3$ (26%), which could be separated by trap-to-trap distillation from the major product. The dimer collects at -70 °C, and $(CF_3)_2NCN$ collects at -110 °C. See ref 5 and 15 for previous spectral data. Data: IR (8 Torr) 2270 (w), 1367 (vs), 1278 (vs), 1238 (vs), 1188 (m), 1159 (m), 947 (s), 730 (m) cm^{-1}; ^{19}F NMR (C_6D_6) $\delta(CF_3) = -58.2$ (s).

$CF_3N(F)C=N$. A 60% yield was obtained for 2.3 mmol of $CF_2=NF$ and 2.4 mmol of FCN over 17 mmol of KF with 0.2 mmol of $(CF_3)_2N$-CN as the only side product. $(CF_3)_2NCN$ was retained in a -110 °C trap, $CF_3N(F)CN$ was retained in a -125 °C trap, and some unreacted $CF_2=NF$ (0.6 mmol) was recovered in a ~196 °C trap. Data: bp -18.2 °C; mp < -155 °C; log P (Torr) = 7.477 - (1171.7/T); ΔH_{vap} = 5.36 kcal/mol; ΔS_{vap} = 21.0 eu; IR (10 Torr) 2243 (w), 1389 (w), 1295 (vs), 1246 (vs), 1089 (m), 984 (m), 788 (w), 674 (w) cm^{-1}; ^{19}F NMR (C_6D_6) $(CF_3^MN(F^A)CN$, AM_3 spin system) δ -52.2 (q, A), -71.9 (d, M), J_{AM} = 18.3 Hz; MS (CI) m/z 129 (MH$^+$, 100%), 128 (M$^+$), 109 (M - F)$^+$, 91 (MH$^+$ - 2 F), 90 (M - 2 F)$^+$, 69 (CF$_3$)$^+$; MS (EI) m/z 128 (M$^+$), 109 (M - F)$^+$, 97 (M - CF)$^+$, 90 (M - 2 F)$^+$, 83 (CF$_3$N)$^+$, 69 (CF$_3^+$, 100%).

$CF_3N(F)CF=NCF_3$ and $CF_3NCF_2NCF_3$. By the reaction of 3.4 mmol of $CF_3N=CF_2$ and 3.4 mmol of $CF_2=NF$ over 17 mmol of KF, the two isomers were obtained in 95% overall yield. Fractional distillation of the volatile products after 5-h reaction time yielded 1.8 mmol of $CF_3N(F)$-CF=NCF$_3$ (40%) in the -82 °C trap and 1.3 mmol of $CF_3NCF_2NCF_3$ (55%) in the -130 °C trap. The -196 °C trap contained 0.4 mmol of unidentified products of lower molecular weight. (Although repetition of these reaction conditions produced comparable overall yields, the relative yield of diaziridine increased to as high as 72%, depending on the specific history of the KF sample employed.)

$CF_3N(F)CF=NCF_3$: bp 31.8 °C; mp < -125 °C; log P (Torr) = 8.011 - (1663.0/T) - (30078/T^2); ΔH_{vap} = 6.71 kcal/mol; ΔS_{vap} = 22.0 eu; IR (9 Torr) 1763 (vs, C=N), 1391 (s), 1325 (vs), 1268 (vs), 1219 (vs), 1074 (m), 1023 (m), 1001 (s), 867 (w), 839 (m), 747 (w), 685 (m), 655 (w) cm^{-1}; MS (CI, major) m/z 217 (MH$^+$), 216 (M$^+$), 198 (MH$^+$ - F), 197 (M - F)$^+$, 179 (MH$^+$ - 2 F), 178 (M - 2 F)$^+$, 159 (M - 3 F)$^+$, 129, 128, 114, 109, 85 (CF$_3$CN)$^+$, 69 (CF$_3$)$^+$; MS (EI) m/z 216 (M$^+$), 197 (M - F)$^+$, 178 (M - 2 F)$^+$, 159 (M - 3 F)$^+$, 128 (NCFNCF$_3$)$^+$, 114

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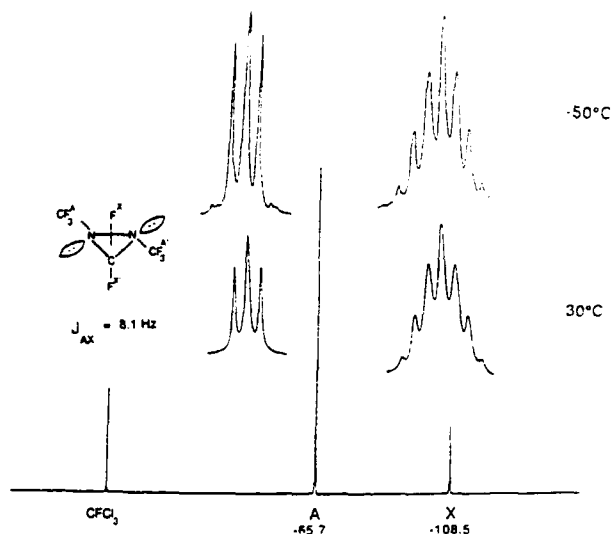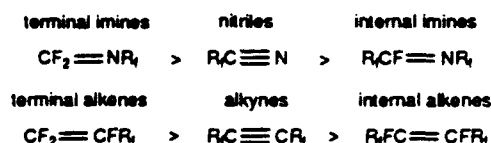

Figure 1.

$(CFNCF_3)^+$, 109, 69 (CF$_3^+$, 100%); ^{19}F NMR $(CF_3^MN(F^A)CF^Y=$ NCF$_3^X$, AM$_3$X$_3$Y spin system) δ -35.7 (d, q, q, A), -54.8 (d, M), -68.0 (d, d, m, X), -70.5 (d, q, m, Y), $J_{AM} = J_{XY} = J_{MY}$ = 12 Hz, J_{AY} = 52 Hz, $J_{AX} = J_{MX} \leq$ 2 Hz.

$CF_3NCF_2NCF_3$: bp -0.2 °C; mp < -155 °C; log P (Torr) = 8.972 - (1984.0/T) - (87743/T^2); ΔH_{vap} = 6.14 kcal/mol; ΔS_{vap} = 22.4 eu; IR (2 Torr) 1443 (s), 1318 (s), 1279 (s), 1246 (vs), 1206 (vs), 1115 (w), 997 (m), 846 (w), 680 (m) cm^{-1}; MS (CI, major) m/z 217 (MH$^+$), 216 (M)$^+$, 198 (MH$^+$ - F), 197 (M - F)$^+$, 167 (MH$^+$ - CF$_2$), 166 (M - CF$_2$)$^+$, 150, 147 (M - CF$_3$)$^+$, 129, 128, 114 (C$_2$F$_4$N)$^+$, 109, 69 (CF$_3$)$^+$; MS (EI) m/z 216 (M$^+$), 128, 114 (C$_2$F$_4$N)$^+$, 109, 69 (CF$_3$)$^+$; ^{19}F NMR $(A_6X_2$ spin systems) δ_A -65.7 (t, CF$_3$), δ_X -108.6 (sept, CF$_2$), J_{AX} = 8.1 Hz (see Figure 1 for NMR spectra, 30 and -50 °C).

General Procedure for N,N-Dichloramine Syntheses. The nitriles were condensed into a 20-mL FEP tube fitted with a stainless steel valve. ClF was added in slight excess of a 2:1 molar ratio, and the mixture was allowed to warm from -196 to +25 °C in a cool Dewar flask. The volatiles were transferred to the glass fractionation train where excess ClF was separated from the dichloramines.

$(CF_3)_2NCF_2NCl_2$. An 81% yield was obtained from 1.0 mmol of $(CF_3)_2NCN$. The dichloramine was collected in a -110 °C trap. Data: IR (6 Torr) 1341 (vs), 1276 (s), 1225 (vs), 1192 (s), 1121 (s), 993 (vs), 971 (vs), 831 (w), 733 (m), 682 (w), 639 (w) cm^{-1}; MS (CI) m/z 291/289/287 (MH$^+$), 271/269/267 (M - F)$^+$, 253/251 (M - Cl)$^+$, 235/233 (MH$^+$ - ClF), 203 (MH$^+$ - NCl$_2$), 202 (M$^+$ - NCl$_2$, 100%), 152 (C$_2$F$_6$N)$^+$, 138/136/134 (CF$_2$NCl$_2$)$^+$, 114 (C$_2$F$_4$N)$^+$; MS (EI) m/z 290/288/286 (M$^+$), 271/269/267 (M - F)$^+$, 234/232 (M - ClF)$^+$, 202 (M$^+$ - NCl$_2$, 100%), 138/136/134 (CF$_2$NCl$_2$)$^+$, 114 (C$_2$F$_4$N)$^+$, 69 (CF$_3^+$); ^{19}F NMR (C_6D_6) $((CF_3^A)_2NCF_2^XNCl_2$, A$_6$X$_2$ spin system) δ -54.2 (t, A), -78.5 (sept, X), J_{AX} = 12.7 Hz.

$CF_3N(F)CF_2NCl_2$. A 41% yield was removed from 0.5 mmol of $CF_3N(F)CN$. The dichloramine was retained in a -125 °C trap. Data: IR (6 Torr) 1289 (vs), 1242 (vs), 1180 (s), 1147 (s), 1035 (m), 955 (m), 839 (w), 780 (w), 687 (m) cm^{-1}; MS (CI) m/z 241/239/237 (MH$^+$), 221/219/217 (M - F)$^+$, 203/201 (M$^+$ - Cl), 185/183 (MH$^+$ - ClF), 184/182 (M - ClF)$^+$, 169, 156, 154, 152 (C$_2$F$_6$N$^+$), 147, 145, 138/136/134 (CF$_2$NCl$_2$)$^+$, 129, 120/118 (CF$_3$NCl)$^+$, 114 (C$_2$F$_4$N)$^+$, 102 (CF$_3$NF)$^+$; MS (EI) m/z 184/182 (M$^+$ - ClF), 153 (CF$_3$NFCF$_2$H)$^+$, 152 (CF$_3$NFCF$_2$)$^+$, 138/136/134 (CF$_2$NCl$_2$)$^+$, 120/118 (CF$_3$NCl)$^+$, 114 (C$_2$F$_4$N)$^+$, 101/99 (CF$_2$NCl)$^+$, 88/86/84 (NCl$_2$)$^+$, 83 (CF$_3$N)$^+$, 77, 69 (CF$_3^+$, 100%), 51/49 (NCl$^+$); ^{19}F NMR (CDCl$_3$) $(CF_3^AN(F^M)$-CF$_2^XNCl_2$, A$_3$MX$_2$ spin system) δ -69.0 (d, t, A), -83.3 (br t, q, M), -91.8 (d, q, X), J_{AM} = 13.8 Hz, J_{AX} = 11.6 Hz, J_{MX} = 17.4 Hz.

Other Derivatives. $(CF_3)_2NCF_2NF_2$. Into a 20-mL FEP reactor fitted with a stainless steel valve was placed 1.0 g (7.0 mmol) of CsF. $(CF_3)_2NCN$ (1.0 mmol) and F_2 (3.0 mmol) were condensed into the reactor at -196 °C. The reactor was allowed to warm to 22 °C in a cool Dewar over 6 h, and the excess F_2 (1.7 mmol) was removed by pumping out the reactor while it was cooled to -196 °C. The volatiles were then separated through traps at -110 and -196 °C. The -110 °C trap retained a mixture of $(CF_3)_2NCN$ and $(CF_3)_2NCF_2NF_2$ (~30% yield). The -196 °C volatiles contained a small amount of $(CF_3)_2NF$ and CF_3NF_2, which were identified by comparison with the known IR and ^{19}F NMR spectra.[13,14] The contents of the -110 °C trap were not separated further.

Scheme II

Addition:

$$R_f\text{-CF} + CF_2=CFR_f \longrightarrow R_f\text{-CF-}CF_2\text{-}\bar{C}R_f$$

Elimination:

$$R_f\text{-CF-}CF_2\bar{C}R_f \xrightarrow{-F^-} R_f\text{-CF-}C=CR_f$$

Addition:

$$CF_3\bar{N}\text{-}R_f + CF_2=N\text{-}R_f \longrightarrow R_f\text{-N-CF}_2\bar{N}\text{-}R_f$$

Elimination:

$$R_f\text{-N-CF}_2\bar{N}\text{-}R_f \xrightarrow{-F^-} R_f\text{-N-CF}=N\text{-}R_f$$

Scheme III

$$CF_3\text{-}N=CF_2 \xrightarrow[(1)]{F^-} (CF_3)_2\bar{N}$$

$$\xrightarrow[(3)]{FCN} (CF_3)_2N\text{-}C\equiv N$$
$$\xrightarrow[(4)]{CF_3\text{-}N=CF_2} (CF_3)_2N\text{-}CF=N\text{-}CF_3$$

$$F\text{-}C\equiv N \xrightarrow[(2)]{F^-} CF_2=\bar{N}$$

$$\xrightarrow[(5)]{FCN} (CF_3)_2N\text{-}C\equiv N$$
$$\xrightarrow[(6)]{CF_3\text{-}N=CF_2} \bar{C}F_2=N\text{-}CF=N\text{-}CF_3$$

Scheme IV

$$CF_2=N\text{-}F \xrightarrow[(7)]{F^-} CF_3NF^-$$

$$\xrightarrow[(8)]{FCN} CF_3N(F)\text{-}C\equiv N$$
$$\xrightarrow[(9)]{CF_2=N\text{-}F} CF_3N(F)\text{-}CF=N\text{-}F$$

$$F\text{-}C\equiv N \xrightarrow[(2)]{F^-} CF_2\bar{N}$$

$$\xrightarrow[(5)]{FCN} (CF_3)_2N\text{-}C\equiv N$$
$$\xrightarrow[(10)]{CF_2=N\text{-}F} \bar{C}F_2N\text{-}CF=N\text{-}F^-$$
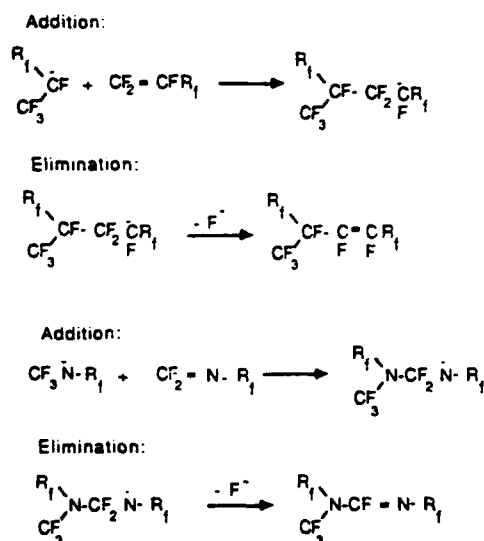
Data: IR (5 Torr, (CF$_3$)$_2$NCN substracted) 1365 (vs), 1310 (m), 1280 (s), 1236 (vs), 1028 (m), 997 (s), 944 (m), 910 (m), 874 (w), 758 (w) cm^{-1}; ^{19}F NMR (C$_6$D$_6$) ((CF$_3^M$)$_2$NCF$_2^X$NF$_2^A$, A$_2$M$_4$X$_2$ spin system) δ 17.4 (br s, A), −53.7 (t, M), −115.4 (sept, X), J_{MX} = 12.2 Hz, J_{AX} < 1 Hz. J_{AM} < 1 Hz.

(CF$_3$)$_2$NCF=NBr. (CF$_3$)$_2$NCN (2.0 mmol) was condensed into a glass reactor previously charged with 1.0 g (7.0 mmol) of CsF. Br$_2$ (10.0 mmol) was added, and the mixture was allowed to stand in the dark for 4–5 days. The volatiles were fractionated through a −90 °C trap to remove any unreacted (CF$_3$)$_2$NCN. The contents of the −90 °C trap were treated with 5.0 mmol of ethylene to remove excess Br$_2$. Fractionation through traps at −50 and −90 °C gave BrCH$_2$CH$_2$Br and (CF$_3$)$_2$NCF=NBr (1.8 mmol, 90% yield), respectively. Data: IR (12 Torr) 1690 (C=N, s), 1374 (vs), 1295 (s), 1274 (s), 1226 (vs), 1028 (w), 998 (m), 703 (w), 638 (w) cm^{-1}; ^{19}F NMR (C$_6$D$_6$) ((CF$_3^X$)$_2$NCF^A=NBr, AX$_6$ spin system) δ −9.4 (sept, A), −56.0 (d, X), J_{AX} = 8.0 Hz; MS (CI, major) m/z 279/277 (MH$^+$), 278/276 (M$^+$), 260/258 (MH$^+$ − F), 259/257 (M − F)$^+$, 242/240, 197 (M − Br)$^+$, 179 (MH$^+$ − BrF), 167 (MH$^+$ − CFBr), 134 (C$_2$F$_5$NH)$^+$, 127/125 (CFNBr)$^+$, 109, 107; MS (EI) m/z 278/276 (M$^+$), 214/212 (M − CF$_2$N)$^+$, 197 (M − Br)$^+$, 190/188 (M$^+$ − CF$_4$), 126/124 (CFNBr)$^+$, 114 (C$_2$F$_4$N)$^+$, 109 (CF$_3$NCN)$^+$, 81/79 (Br$^+$), 69 (CF$_3^+$).

Results and Discussion

General Reactivity of Fluorinated Imines and Alkenes. Reactions of nucleophilic nitrogen-centered anions are important in the development of fluorinated nitrogen compounds. Although the carbanions derived from fluoro olefinic systems are well studied, the nitrogen analogues have received less attention despite their greater reactivity.[15] The general trend for the fluoro olefins is that less substituted olefins are more reactive. Similarly, a parallel order of reactivity for these analogous systems is shown below:

terminal imines	nitriles	internal imines
CF$_2$=NR$_f$ >	R$_f$C≡N >	R$_f$CF=NR$_f$

terminal alkenes	alkynes	internal alkenes
CF$_2$=CFR$_f$ >	R$_f$C≡CR$_f$ >	R$_f$FC=CFR$_f$

Fluoride-promoted substitution of terminal fluoro olefins gives substituted olefins by an addition–elimination sequence.[16] Suitably substituted imines and nitriles react quite readily in an analogous fashion in fluoride-promoted reactions at the imine carbon. Scheme II illustrates the addition–elimination mechanism in both systems.

In order to compare the reactivities of the anions generated by fluoride-catalyzed reactions of FCN, CF$_2$=NF and CF$_3$N=CF$_2$,
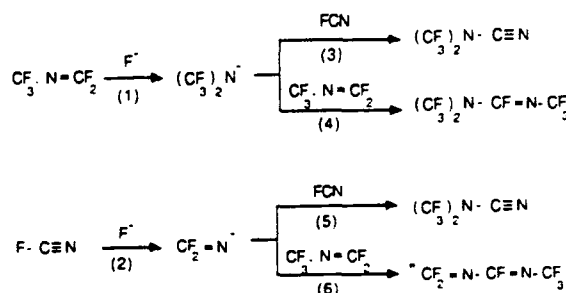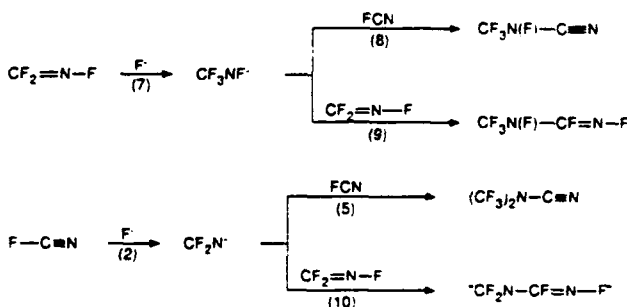
the substrates were combined in pairs over an alkali metal fluoride. The relevant anions in this study were therefore CF$_2$=N$^-$, CF$_3$N(F)$^-$, and (CF$_3$)$_2$N$^-$.

The course of these reactions depends on the relative rates of alkali metal fluoride attack on the imines and nitrile and the relative rates of nucleophilic substitution of the anion(s) formed with the imine and/or nitrile remaining in the gas phase. A comprehensive set of possible substitution reactions is diagrammed in Scheme III for the first competitive reaction between FCN and CF$_3$N=CF$_2$.

Reactions 1 and 2 reflect the relative reactivities of the substrates with fluoride ion while reactions 3–6 relate anion nucleophilicities toward the two free substrates. Since product derived from path 6 was not observed, the contribution to the yield of (CF$_3$)$_2$NCN by path 5 is probably minor as both paths are dependent upon the competitive rate of the preceding path 2. The major products arise from paths 3 and 4, which correspond in yield to 70% and 26% of the CF$_3$N=CF$_2$ initially introduced. This suggests that (CF$_3$)$_2$N$^-$ shows an ~5:1 preference for FCN over its parent imine, CF$_3$N=CF$_2$. Isolation of (CF$_3$)$_2$NCN and (CF$_3$)$_2$NCF=NCF$_3$ as the major products establishes the superior anion formation from CF$_3$N=CF$_2$ over FCN.

The reaction of FCN with itself over KF or CsF has not been reported although fluoride-promoted addition reactions have been investigated.[5] When FCN was allowed to stand over excess KF for 2 h, the only isolated product was (CF$_3$)$_2$NC≡N (approximately 80% of fluorine recovered in the product). Sundermeyer and Schachner found this compound as one of a number of products of the reaction of FCN with COF$_2$ over CsF.[5] Cameron and Tattershall isolated (CF$_3$)$_2$NCN as the major product of the reaction of cyanogen chloride with KF.[17] Minor products included CF$_3$N=CF$_2$ and CF$_3$N=CCl$_2$. We have not isolated CF$_3$N=CF$_2$, presumably an intermediate in the conversion to (CF$_3$)$_2$NCN, from our reaction mixture. The increased carbon to nitrogen ratio from the reactant, FCN (1:1), to the product, (CF$_3$)$_2$NCN (3:2), was noted with interest by the Tattershall group.[17] We have no further mechanistic explanation for this conversion.

In the second competitive reaction, a related set of basic reactions must be compared with the observed products. Scheme IV depicts the possibilities for the reaction of FCN and CF$_2$=NF over KF. Since little (CF$_3$)$_2$NCN is formed and no evidence for

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(14) Ruff, J. K. *J. Org. Chem.* **1967**, *32*, 1675.
(15) Chambers, R. D. *Fluorine in Organic Chemistry*, John Wiley & Sons: New York, 1973; p 247.
(16) See ref 15, p 104.
(17) Cameron, J. D.; Tattershall, B. W. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 166.

Fluoride-Promoted Competitive Reactions

J. Am. Chem. Soc., Vol. 112, No. 2, 1990 731
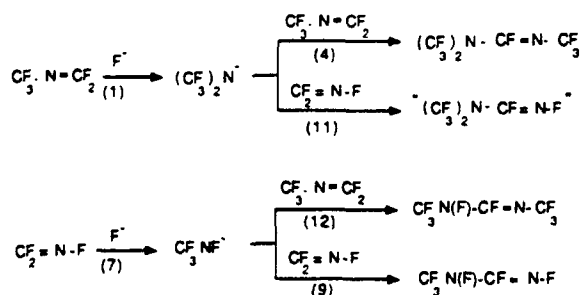
Scheme V

Scheme VI
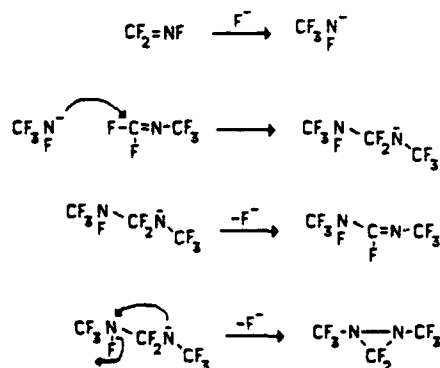
path 10 is observed, reaction 7 producing CF_3NF^- clearly predominates over reaction 2 producing $CF_2=N^-$. The formation of $CF_3N(F)CN$ demonstrates that the anion CF_3NF^- is formed quickly over KF and reacts selectively with FCN rather than $CF_2=NF$. Although one could argue that little free $CF_2=NF$ is available for attack by CF_3NF^-, the reaction of $CF_2=NF$ with KF in the absence of FCN produced a high yield of $CF_3NFC-F=NF$.[4] Path 9 defines this dimerization path. In this reaction, selective anion formation [7 > 2] and selective nucleophilic displacement [8 > 9] generate one product, $CF_3N(F)CN$, in reasonably high yield.

An overview of the third competitive reaction between $CF_2=NF$ and $CF_3N=CF_2$ over KF is diagrammed in Scheme V. The observed products indicate that reaction 7 predominates over reaction 1 in the production of the superior nucleophile, CF_3NF^-. This nucleophile reacts selectively with $CF_3N=CF_2$ rather than $CF_2=NF$. The major products isolated from the reaction are $CF_3N(F)CF=NCF_3$ and the diaziridine $CF_3NCF_2NCF_3$.

The diaziridine forms as a result of fluoride attack on the initially formed adduct and subsequent intramolecular displacement of fluoride from nitrogen as shown in Scheme VI. This rearrangement is analogous to those in related systems,[4,18-20] as shown previously for the conversion of $CF_3N(F)CF=NF$ to CF_3NCF_2NF.[4] Brief exposure of the mixture of isomeric codimers to CsF converted all of the linear adduct to the diaziridine and provided a pure sample of diaziridine.

The structure of 1,2-bis(trifluoromethyl)-3,3-difluorodiaziridine is of interest because of its inherent symmetry. Diaziridines are
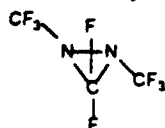
known to favor a trans orientation of the nitrogen substituents in order to reduce repulsion of the two lone pairs.[21] A cis ori-

entation of the substituents would render the methylene fluorines on the ring carbon nonequivalent. In this event, a large coupling between these fluorines should be observable in the ^{19}F NMR spectrum. The ^{19}F NMR spectrum at 20 °C shows two signals coupled by 8.1 Hz. The two CF_3 groups appear as a triplet and the CF_2 fluorines as a septet. This simple, first-order spectrum supports the trans-substituted diaziridine structure.

This structure of C_2 symmetry can be observed to be one of a pair of enantiomers when fixed in a rigid configuration. We have no reason to believe that we have enriched one enantiomer in this reaction because the reactants. $CF_2=NF$ and $CF_3N=CF_2$, are achiral with no chiral component in the reaction medium. Thus, as long as the diaziridine is locked in configuration, a racemic mixture is present.

Because of the strongly electronegative CF_3 substituents on the ring, nitrogen inversion barriers should be unusually high for several reasons.[21] In the first place, nitrogen in a three-membered ring shows hindered inversion relative to an acyclic nitrogen. Furthermore, inclusion of a second heteroatom, nitrogen or otherwise, into a three-membered aza ring further elevates the barrier of inversion for nitrogen. The *gem*-fluorines on the ring carbon of the diaziridine comprise an electronegative substituent for both nitrogens, which hinders inversion rates both in cyclic and acyclic amines.[21,22]

A variable-temperature NMR experiment was performed in order to determine the effect of temperature on the barriers to inversion of the nitrogens in the diaziridine. Although the 30 °C spectrum had revealed fairly sharp resolution for the triplet-septet pattern, the spectrum sharpened further at -50 °C but retained the same peak shapes. See Figure 1. No further change was observed at temperatures as low as -80 °C.

Higher temperatures were explored to test the barrier of inversion since the low-temperature results strongly suggested a ring system locked belows its T_c. The NMR of the diaziridine as a neat gas was run at 30 and 100 °C in a sealed NMR tube with no internal reference. The signals appeared in the same relative position in each spectrum, but resolution was diminished so that precise couplings were not attainable.

The diaziridine shows unexpectedly high thermal stability for a strained, electronegatively substituted ring system. At low pressure in the gas phase, a sample was heated to 320 °C before decomposition was observed by formation of a film within the Pyrex reactor and disappearance of the characteristic IR spectrum of the diaziridine. The mixture of volatile products was not identified.

Heating to 100 °C with $AlCl_3$ for 8 h produced no change in the IR spectrum of the diaziridine, and no reaction was observed between the diaziridine and 100% sulfuric acid.

Derivatives of the Competitive Reaction Products. Most perhalo nitriles can be treated with chlorine monofluoride to yield N,N-dichloramines.[23,24] The addition does not stop at the N-chlorimine stage presumably because the rate of addition of ClF is faster for the intermediate N-chlorimine than for the nitrile. Thus, by a 2-fold addition were the two nitriles derivatized to N,N-dichloramines, as shown below:

$$(CF_3)_2NCN \xrightarrow{2ClF} (CF_3)_2NCF_2NCl_2$$

$$CF_3N(F)CN \xrightarrow{2ClF} CF_3N(F)CF_2NCl_2$$
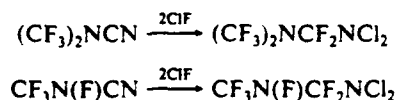
The two N,N-dichloramines are not sensitive to sunlight. Reaction of $(CF_3)_2NCF_2NCl_2$ with CsF and Br_2 did not product an N-bromo compound as was observed earlier in the conversion of CF_3NCl_2 to CF_3NBrCl and CF_3NBr_2.[25]

The reaction of perhalo nitriles with CsF and Br_2 is a demonstrated method for synthesizing N-bromimines.[7] The reaction

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Scheme VII

$$F_2N-C\equiv N \xrightarrow{CsF} F_2C\begin{smallmatrix}N\\\|\\N\end{smallmatrix}$$

$$F_2N-C\equiv N \xrightarrow{F^-} F_2N-\underset{\underset{N}{\|}}{C}-F$$

$$\downarrow -F^-$$

$$F-N-CF_2 \xleftarrow{F^-} F-N-C-F$$

Scheme VIII

$$CF_3\underset{F}{N}-C\equiv N \xrightarrow{CsF} CF_3N=CF_2 + CF_3-N-CF_2 + 1/2 N_2 + \cdots$$

$$CF_3\underset{F}{N}-C\equiv N \xrightarrow{F^-} CF_3\underset{F}{N}-C-F$$
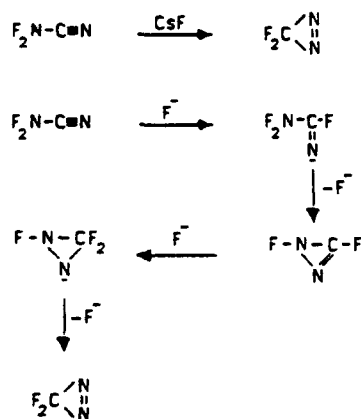
of $(CF_3)_2NC\equiv N$ with CsF and Br_2 provides $(CF_3)_2NCF=NBr$. Further oxidation of *N*-bromimines to the *N,N*-dibromamines has been reported for some substituted nitriles,[25,26] but $(CF_3)_2NC$-$F=NBr$ was not oxidized further. The steric influence of the $(CF_3)_2N$ group may prevent the attack of the fluoride base on the imine carbon. Exhaustive addition of fluorine to $(CF_3)_2N$-$C\equiv N$ was accomplished by reaction with CsF and F_2, but only in conjunction with a side reaction that severed the N–CN bond. The observed product mixture for this reaction is shown below:

$$(CF_3)_2NCN \xrightarrow[F_2]{CsF} (CF_3)_2NCF_2NF_2 + (CF_3)_2NF + CF_3NF_2$$

Decomposition of $CF_3N(F)CN$ over CsF. The CsF-promoted isomerization of difluorocyanamide, $F_2NC\equiv N$, led to the diaziridine, $\overline{CF_2N=N}$.[19,20] Scheme VII illustrates the proposed mechanism, which invokes fluoride attack on the nitrile carbon to produce a nitrogen anion. This anion undergoes an intramolecular nucleophilic attack on the NF_2 group to yield a 2-diazirine that rearranges to the more stable 1-diazirine by successive gain and loss of a fluoride ion.

The reaction of $CF_3N(F)C\equiv N$ with CsF bears a similarity to that of $NF_2C\equiv N$. The anticipated pathways in this reaction are shown in Scheme VIII. Attempts to pump off the intermediate diazirine were unsuccessful. Among the volatile products of the reaction were $CF_3N=CF_2$, nitrogen, and *N*-fluorodiaziridine ($CF_2=NF$ dimer). The remaining cesium salts displayed a bright yellow color, which indicated that some material remained behind as salts or oligomeric byproducts. The reactive intermediate diazirine shown in Scheme VIII may absorb fluoride ion to produce a diaziridine anion. Our failure to isolate the intermediate diazirine speaks for the apparent instability of the diaziridine anion.

A related azirine, $CF_3\overline{CF=CF=N}$, was reported by Krespan to polymerize in the presence of fluoride ion.[27] This azirine is unstable but decomposes without loss of nitrogen. The mechanism of the decomposition of $CF_3N(F)CN$ is clearly not a simple, uniform process. Several pathways may lead to the consumption of the *N*-cyanoamine, not all of which involve the diaziridine anion as the final intermediate.

Competitive Reactions of Nitrogen-Based Anions. Several considerations are significant in determining the usefulness of fluoride-promoted competitive reactions of nitrogen-based anion. One important limitation is the favored dimerization of fluorinated terminal imines. $CF_2=NF$ and $CF_3N=CF_2$ represent not only two of the most desirable anion sources but also two of the most easily dimerized imines. In order to gain advantage from competitive reactions, attack by the desired nitrogen anion on the coreactant imine must predominate over the pathways leading to dimerization and side products.

For general use with difluoromethylenimino systems, the nucleophilic attack of a nitrogen anion on the imine carbon is the
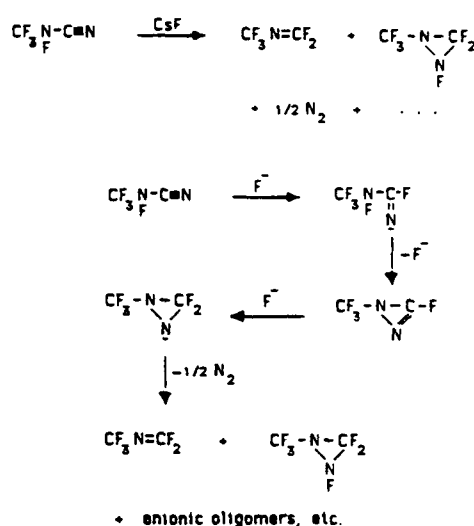
critical step. Unfortunately, a competitive side reaction for many terminal imines is conversion to a much less reactive internal aimine by successive gain and loss of fluoride ion. In fact, only terminal imines lacking a fluorine on the α-carbon are completely exempt from this limitation. The sole exception is $CF_3N=CF_2$, which undergoes a degenerate fluoride ion isomerization, thereby maintaining its integrity as a terminal imine. This unique isomerization is illustrated below:

$$CF_2=NCF_3 \overset{F^-}{\rightleftharpoons} (CF_3)_2N^- \overset{-F^-}{\rightleftharpoons} CF_3N=CF_2$$
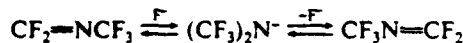
As has been found in this study, the observed order of anion reactivity for these three substrates is
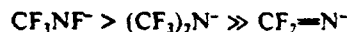
$$CF_3NF^- > (CF_3)_2N^- \gg CF_2=N^-$$

The nucleophilic anions, CF_3NF^- and $(CF_3)_2N^-$, display differing selectivities in attacking neutral substrates. While CF_3NF^- attacks FCN or $CF_3N=CF_2$ preferentially over $CF_2=NF$, $(CF_3)_2N^-$ selects FCN over its parent imine, $CF_3N=CF_2$, in a ~5:1 ratio. These results are consistent with previous studies of CF_3NF^- with acyl fluorides[4] and studies of SF_5NF^- with acyl fluorides and $CF_2=NF$, in which SF_5NF^- was even more reactive than CF_3NF^-.[28]

An imine candidate for fluoride-promoted competitive reactions must possess reactive acyl-type fluorines that can be displaced by an active nucleophile. Terminal imines are sufficiently reactive with nucleophiles, as long as they are not readily rearranged by fluoride. For a viable terminal imine system, $CF_2=N=R_f$, the expected reactions with each of the substrates of this study are shown below.

$$CF_3NF^- + CF_2=NR_x \xrightarrow{-F^-} CF_3NFCF=NR_x$$

$$(CF_3)_2N^- + CF_2=NR_x \xrightarrow{-F^-} (CF_3)_2NCF=NR_x$$

$$CF_3N^-R_x + FCN \xrightarrow{-F^-} R_xN(CF_3)CN$$
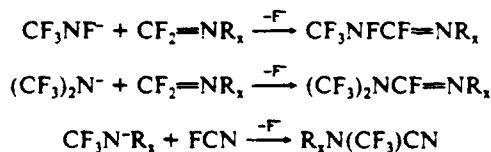
The two reactions with $CF_2=NF$ and $CF_3N=CF_2$ involve simple displacements of fluoride from the terminus of the less reactive imine by the strong nucleophiles CF_3NF^- and $(CF_3)_2N^-$. In the third example, the anion generated by the competing imine should serve as a nucleophile in displacing fluoride ion from FCN.

Reactions of competing imines can be utilized for intermolecular additions if the nitrogen anion of the one component is nucleophilic enough to displace fluoride from the other substrate. The coreactant must contain an electrophilic center that will not undergo a facile fluoride 1,3-shift under the reaction conditions. The nucleophiles that have demonstrated their efficiency in this mode

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of reaction are CF_3NF^- and $(CF_3)_2N^-$. $CF_2=N^-$ is consistently defeated as a nucleophile, but FCN can be used as an electrophilic substrate with a suitably nucleophilic anion. The list of imines that have been successfully attacked by CF_3NF^- includes the $CF_2=NX$ series (X = F, Cl, Br)[4,18,29] and $CF_3N=CF_2$, but other qualified substrate imines should behave similarly.

Alkali metal fluoride promoted reactions of the other N-halodifluoromethylenimines, $CF_2=NX$ (X = Cl, Br), offer little evidence of nucleophilic anions like CF_3NF^-. Neither the CF_3NCl^- anion near the CF_3NBr^- anion, both far less stable over the metal fluoride surface, have reacted nucleophilically with any of the substrates that we have examined.[18]

In summary, the competitive reactions of the perfluorinated imines, $CF_2=NF$ and $CF_3N=CF_2$, and FCN in the presence of KF and CsF generate new compounds that include fluorinated N-cyano compounds and a stable symmetric diaziridine. These reactions establish a relative order of reactivity for these substrates with alkali metal fluoride and the corresponding order of nucleophilicity for the related anions. Some derivatives of the N-cyano compounds, including two N,N-dichloramines and an N-bromimine, have been synthesized.

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CESIUM FLUORIDE-ASSISTED REACTIONS OF SYN AND ANTI N-FLUORO-1-CYANO-1-FLUOROMETHANIMINE WITH CHLORINE AND BROMINE [1]

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SUMMARY

The CsF-assisted reactions of **syn** and **anti**- $NCCF=NF$ with Cl_2 and Br_2 and the uncatalyzed addition of ClF are described. Chlorine reacts only with the imine function, whereas Br_2 reacts with both carbon-nitrogen multiple bonds. The more reactive **syn** isomer is isomerized to the **anti**-isomer under the reaction conditions. Six new compounds are reported and their structures assigned by ^{19}F NMR and infrared spectroscopy: $Cl_2NCF_2CF_2NClF$ **I**, $NCCF_2NClF$ **II**, $NCCF_2NFBr$ **III**, **syn** - $BrN=CFCF=NF$ **IV**, **syn** - $Br-N=CFCF_2NBrF$ **V**, and **syn** - $BrN=CFCF_2NClF$ **VI**.

INTRODUCTION

The synthesis and reactivity of fluorinated imines and nitriles have been of renewed interest in the last ten years, especially concerning their oxidations with halogen fluorides and related compounds to novel N-

halogen derivatives [2] and with peroxides to oxaziridines [3]. More recently, the fluoride-assisted bromination and chlorination of nitriles and imines has provided routes to a variety of new N-halogen compounds [4-6] and the discovery of the metal fluoride-promoted conversion of N-Cl bonds to N-Br bonds further expanded the variety of N-halogen species obtainable [7,8]. Methods are now available for the facile synthesis of $R_fCF=NX$ and R_fNXX' ($X,X'=F,Cl,Br$).

As an extension of this work, we wanted to investigate the reactivity of a compound containing both a C-N double and a triple bond. The candidate selected was $N\equiv CCF=NF$ [9], readily available from $CF_2=NF$ [10] as a mixture of syn and anti isomers. The reactions with Cl_2 and Br_2 in the presence of CsF and with ClF are described.

EXPERIMENTAL SECTION

General Methods. Volatile compounds were handled in a Pyrex or stainless steel (304 and 316) vacuum system equipped with a Wallace and Tiernan Series 1500 differential pressure gauge. Gaseous materials were measured with the assumption of the ideal gas law. Nonvolatile materials were weighed. ^{19}F NMR spectra were obtained on a JEOL FX-90Q spectrometer operating at 84.3 MHz. All chemical shifts are reported relative to internal CCl_3F. The usual solvent was ~80 mole % CCl_4 and ~20 mole % $CDCl_3$. Infrared spectra were recorded on a Perkin-Elmer 1430 spectrometer connected to a 3600 data station. A 10-cm glass cell fitted with KCl windows was employed. Mass spectra were taken on a HP 5985-B GC/MS instrument at 15 eV for EI and 50 eV for CI (CH_4). Samples were

introduced by direct gas injection. M. p. were taken using a modified Stock procedure.

Reagents. The chemicals Br_2, Cl_2, CsF, and KCN were obtained from commercial sources. The compounds $CF_2=NF$ [10], HCN [11], and $NCCF=NF$ [9,12] were prepared by literature methods. Chlorine monofluoride was prepared by reaction of equimolar amounts of Cl_2 and F_2 in a Monel bomb at 250°C.

Reactions. Compounds II-VI were prepared in 100-ml glass bulbs fitted with a glass-Teflon valve. Cesium fluoride which had been fused and ground to a fine powder in a dry box was added to the reactor in the dry box. The reactor was then evacuated, cooled to -196°C, and the gaseous reactants were added by vacuum transfer. The reactor was then allowed to warm up to an appropriate temperature for an appropriate time (Table I). After the reaction, any non-condensible gases were removed by vacuum after cooling the reactor to -196°C, and the remaining volatile materials were separated by fractional condensation through a series of cold traps. Compound I was prepared in a 30-ml Hoke stainless steel vessel equipped with a stainless steel valve. A stainless steel vacuum line was used for transferring the reactants ClF and NCCF=NF in a mole ratio of 3:1. The reactor was allowed to warm gradually from -196°C to -50°C over a 2 hour period. The products of the reaction were separated by fractional condensation giving ~58% compound I [13] and ~40% compound II. The reactions are summarized in Table I and the characterization of the new compounds is given below.

$Cl_2NCF^{A'}F^{B'}CF^AF^BNClF^X$ (I): NMR (second-order A'B'AB- type). δ -106.8 (m,A), -98.6 (m,B), -97.7 (m,A'), -92.6 (m,B'), -5.2 (br s, X); J_{AB}=195.3,

$J_{A'B'}$=180.6, J_{BX}=34.2, J_{AX}=2.3, $J_{B'X}$=14.6, $J_{A'X}$=0 Hz; IR 1293 (m), 1219 (vs), 1202 (vs), 1149 (vs), 1138 (vs), 1052 (s), 1025 (s), 927 (m), 889 (m), 786 (m), 740 (s) cm^{-1}; MS (EI), major m/z 252/254/256/258 (M$^+$), 184/186/188 ($Cl_2NCF_2CF_2^+$), 130/132 ($CFCFNFCl^+$), 99/101 (CF_2NCl^+), 49/51 (NCl^+).

$NCCF^AF^BNClF^X$ (II): NMR (second-order ABX-type) δ -86.5 (m,A), -82.9 (m,B), 0.99 (br s,X); J_{AB}=220, J_{AX}=14.7, J_{BX}=29.3Hz; IR 2264 (m), 1219 (vs), 1212 (vs) 1189 (s), 1184 (s), 1118 (s), 922 (m), 838 (m), 832 (m), 735 (w), 690 (w) cm^{-1}. MS (CI), major m/z 145/147 (MH$^+$), 125/127 ($NCCF_2NCl^+$) 118/120 (CF_2NFCl^+), 107/109 (MH$^+$-2F), 91 (MH$^+$-FCl), 76 ($NCCF_2^+$); M.p < -110°C.

$NCCF^AF^BNBrF^X$ (III): NMR (second-order ABX-type) δ -84.4 (m,A), -81.2 (m,B), -10.5 (br s,X); J_{AB}=223, J_{AX}=24.4, J_{BX}=36.6 Hz; IR 2261 (m), 1215 (s), 1202 (vs), 1177 (m), 1107 (s), 967 (w), 919 (m), 809 (w), 680 (w) cm^{-1}. MS (EI), major m/z 188/190 (M$^+$), 124/126 ($FCNBr^+$), 105/107 ($NCBr^+$), 90 ($NCCFNF^+$) 76 ($NCCF_2^+$).

$BrN=CF^MCF^A=NF^X$ (IV): NMR (AMX-type) δ -23.9 (d,d,M), -75.9 (d,d,A) -14.6 (br d, X); J_{MX}=5.2, J_{MA}=17.4, J_{AX}=39.6 Hz; IR 1664 (s), 1367 (m), 1240 (w), 1211 (m), 1161 (s), 979 (s), 758 (m), 735 (w), 662 (m) cm^{-1}. MS (EI), major m/z 188/190 (M$^+$), 174/176 (M-N$^+$), 169/171 (M-F$^+$), 109 (M-Br$^+$).

$BrN=CF^MCF^AF^BNBrF^X$ (V): NMR (ABMX-type) δ -96.7 (m,A), -94.1 (m,B), -20.4 (d,t,M) -16.2 (br s, X); J_{AB}=190.5, J_{AX}=19.5, J_{BX}=39.1, J_{BM}=12.2, J_{AM}=J_{MX}=6.1 Hz; IR 1690 (s), 1306 (s), 1216 (s), 1146 (s), 1080 (s), 916 (m), 742 (m), 674 (w), 658 (w), 637 (w) cm^{-1}; MS (CI) major m/z 287/289/291 (MH$^+$), 267/269/271 (M-F$^+$), 189/191 (MH$^+$-BrF), 174/176 ($BrNCFCF_2^+$), 169/171 ($BrNCFCFN^+$), 124/126 ($BrNCF^+$), 109 ($NCCF_2NF^+$), 93/95 (BrN^+); M.p -18°C.

$BrN=CF^MCF^AF^BNClF^X$ (VI): NMR of a mixture of V and VI gives discrete peaks for F^A, F^B, and F^X due to compound VI. The F^M in compound (V)

has δ at -20.1 ppm which overlaps with the F^M in (VI) (δ = -20.4 ppm) giving rise to an octet pattern with intensity ratios 1:2:2:3:3:2:2:1, with $J_{MX} = J_{MA} = 1/2\ J_{MB}$ = 6.1 Hz. Other resonances for (VI) occur at δ -100.7 (m,A), -96.8 (m,B), -6.1 (br s, X); J_{AB} = 188.3, J_{AX} = 15.3, J_{BX} = 26.9 Hz. The intensity of the NMR signals indicate the ratio of compounds (VI) to (V) is approximately 1. IR of the mixture is essentially the same as (V). MS (CI) gives a base peak corresponding to molecular ions of (VI) m/z 243/245/247 (MH$^+$), 174/176 (BrNCFCF$_2$)$^+$, 130/132 (FCCF$_2$NCl)$^+$, 124/126 (NBrCF)$^+$.

RESULTS AND DISCUSSION

Previously, NCCF=NF was shown to undergo facile nucleophilic substitution of the methylene fluorine [9]. As expected, we found no reactivity of the compound with the weak electrophiles Br$_2$ and Cl$_2$ alone. This is consistent with previous work where CF$_2$=NX, R$_f$CF=NX (X=F, Cl, Br) and R$_f$CN were essentially inert to Cl$_2$ and Br$_2$ [4-8,14]. In contrast, and as expected, NCCF=NF reacts readily with the more electrophilic halogen source ClF as shown (see Table 1).

$$\text{NCCF=NF} \xrightarrow{\text{ClF}} \text{Cl}_2\text{NCF}_2\text{CF}_2\text{NFCl} \quad \text{I} + \text{NCCF}_2\text{NClF} \quad \text{II}$$

A large number of reactions of ClF with a variety of >C=N- and -C≡N compounds, as well as a number of examples with strong halogen electrophiles such as FSO$_2$OX (X=Cl, Br), have shown this to be a general high-yield reaction [2,4,15]. In this case, with ClF, there is an apparent differentiation in reactivity of the C=N versus the C≡N bond. This is

For the first step in the oxidation of the nitrile, a similar sequence can be proposed, i.e.

$$R_fCN + F^- \xrightarrow{\text{CsF}} R_fCF=N^- \xrightarrow{X_2} R_fCF=NX + X^-$$
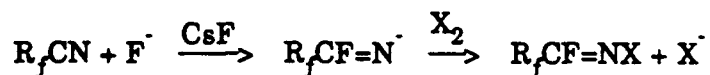
However, it is difficult to reconcile the apparent difference in reactivity of Br_2 -vs- Cl_2 for NCCF=NF if this is the only consideration.

For Br_2, the results in Table 1 do not give a clear differentiation in the relative reactivity of the double and triple bonds, but the imine function appears to be more reactive. Whereas certain nitriles are oxidized to the N,N- dibromo derivative [6,8]. these reactions are usually slow at 22°C [5] and thus no -NBr$_2$ products are observed under the conditions employed in this work. The formation of V in the reaction of II with Br_2 is clearly due to the fluoride-promoted conversion of an N-Cl bond to an N-Br bond as has been previously observed for NCl$_2$ species [7,8].

The structural characterization of compounds I - VI is straightforward from the data given in the experimental section. Intense parent ions could be observed for each compound in the EI or CI mass spectrum with the expected isotopic ratios for chlorine and bromine. The infrared spectra show characteristic υ (C≡N) for II and III at ~2260 cm^{-1} and υ (C=N) for IV - VI at 1660 - 1690 cm^{-1}. Strong υ (C-F) bands are seen in each compound in the 1100 - 1300 cm^{-1} region and bands for υ (N - X) are apparent for N-F (1000 - 900 cm^{-1}) and N-Cl and N-Br (800 - 650 cm^{-1}) but these frequencies cannot be readily assigned with the available data [8].

The ^{19}F NMR provides convincing proof of structure for each compound. Compounds I - III exhibit characteristic ABX patterns for the A -$CF^AF^BNXF^X$ moiety as found for many related molecules, with $J_{AB} \simeq 200$ Hz [19]. Interestingly, the fluorines of the $Cl_2NCF^{A'}F^{B'}$ - group in I are also diastereotopic due to the more distant chiral -NClF group, but there is essentially no ^3J coupling between A'B' and AB fluorines. Compound IV exhibits an AMX spin system where it can be argued that the configuration is **cis-cis**. J_{AX} is only 40 Hz and F^A must therefore be **cis** to X*. Similarly, the chemical shift of F^M at δ -24 indicates M is **cis** to Br**.

Finally, for V and VI an ABMX spin system is observed with a large J_{AB} value similar to I - III and a δ F^M = -20, indicating M is **cis** to Br.

CONCLUSION

Reactions of NCCF=NF with ClF, Cl_2/CsF and Br_2/CsF demonstrate that the imine double bond is more reactive than the nitrile triple bond, allowing selective halogenation to $NCCF_2NXF$ under mild reaction conditions. Both functions can be halogenated with ClF and Br_2/CsF with

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*In
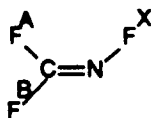
, J_{AX} = 22.1 and J_{BX} = 184 Hz. See references 9 and 12 and references therein.

**In
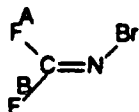
, $δ_A$ = -31.3 and $δ_B$ = -54.3 and in a variety of
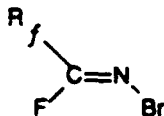
δ(F) $\simeq$ -20. See references 5, 6 and 13 and references therein.

ClF converting the nitrile function to the N,N-dichloroamine and Br_2/CsF only to the N-bromoimine, whereas Cl_2/CsF was unreactive under all conditions tried with the nitrile function. Methods are now available for synthesis of a remarkable number of the possible halogenated derivatives of cyanogen of the type $XX'NCF_2CF_2NXX'$ and $X'N=CFCF=NX$ and $XN=CFCF_2NXX'$ (X,X'=F, Cl, Br).

ACKNOWLEDGMENT

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Cesium Fluoride Promoted Halogenation of Cyanogen by Chlorine and Bromine and Selected Reactions of Products[1]

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The reaction of cyanogen with Cl_2 and Br_2 in the presence of CsF gives rise to a series of compounds, NCCF=NX (Cl. Br), XN=CF—CF=NX (Br), and $NCCF_2NX_2$ (Cl). Subsequent reactions of $NCCF_2NCl_2$ with MF/Br_2 (M = Cs, K, Na) give rise to X'N=CFCF=NX, $XN=CFCF_2NXX'$, and $NCCF_2NXX'$ (X, X' = Cl, Br), involving oxidation and exchange of Cl by • Br. Fourteen compounds were identified by ^{19}F NMR and mass spectrometry, and 10 of the compounds have not been previously reported. Photolysis of NCCF=NX and $NCCF_2NXX'$ gives rise to the respective azine and diazene. The azine undergoes a fluoride ion induced cyclization to form a novel cyclic, 4-membered diazo compound. Thermal additions of NCCF=NBr with C_2F_4 and CF_2=CCl_2 produced only traces of the expected adducts. New compounds identified were NCCF=NCl (1), $NCCF_2NCl_2$ (2), NCCF=NBr (4), $NCCF_2NBrCl$ (14), $NCCF_2NBr_2$ (15), NCCF=N—N=CFCN (16), $NCCF_2N=NCF_2CN$ (17), and NCCFN=NCFCN (18), and ClN=CFCF=NBr (7), BrN=CFCF₂NCl₂ (9), BrN=CFCF₂NClBr (10), ClN=CFCF₂N-ClBr (11), and ClN=CFCF₂NBr₂ (12), which could only be identified in a mixture. Some evidence for NCCF=NC₂F₄Br (19) and NCCF=N(CF₂CCl₂)Br (20) was also found in the addition of 4 to the respective alkenes. Alternative routes to the previously known compounds BrN=CFCF=NBr (5), ClN=CFCF=NCl (6), $Cl_2NCF_2CF_2NCl_2$ (3), ClN=CFCF₂NCl₂ (8), and BrN=CFCF₂NBr₂ (13) were also identified.

Introduction

Cesium fluoride has been shown to be an effective reagent for the fluoride-promoted oxidation of R$_f$CF=NF by Cl_2 and Br_2 to form R$_f$CF$_2$NFX, of R$_f$CN to R$_f$CF$_2$NCl$_2$ and R$_f$CF=NBr,[2,3] of R$_x$N=CF$_2$ to R$_x$N(X)CF$_3$,[4] of CF$_2$=NX' (X' = F, Cl, Br) to CF$_3$NX'X,[2,5,4] of R$_f$CN by F$_2$ to R$_f$CFNF$_2$,[7] and of certain hindered imines R$_f$N=CFR$_f$' by ClF to R$_f$NClCF$_2$R$_f$'.[8] These reactions are quite general with fluorinated imines and nitriles and are believed to occur via intermediate anions R$_f$CF=N$^-$, R$_f$NX$^-$, and R$_x$NCF$_3^-$, although in most instances definitive evidence for the proposed anion intermediates is lacking. In an interesting extension of these fluoride-promoted reactions, we

examined the reactivity of N≡CCF=NF and found both multiple bonds were oxidized by Br_2 but only the imine function was reactive with Cl_2.[9] This work prompted us to examine the reactions of cyanogen under similar conditions to compare the reactivity of Cl_2 and Br_2 and to see if a selective and stepwise oxidation of the triple bonds was possible.[10] Of the 49 structural isomers possible in X₂NCF₂CF₂CF₂NX₂, XN=CFCF=NX, XN=CFCF₂NX₂, NCCF₂=NX₂, and NCCF=NX for combinations of chlorine bromine and fluorine, at least 24 have now been positively identified.

Experimental Section

General Methods. All work was carried out in a conventional Pyrex vacuum system equipped with glass—Teflon valves. Pressures were measured on a Wallace and Tiernan Series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements.

IR spectra were taken on a Perkin-Elmer 1430 spectrometer connected to a 3600 data station using a 10-cm gas cell fitted with KCl windows and a glass—Teflon valve. ^{19}F NMR spectra were taken on a Jeol-FX-90Q Fourier transform spectrometer with ~80 mol % CCl₄ as solvent and ~20 mol % CDCl₃ as internal lock. CFCl₃ was used as an internal

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reference. Chemical shifts are negative to higher field of CFCl₃. Mass spectra were taken on a HP 5985B GC/MS instrument at 15 eV for EI and 50 eV for CI (CH₄). Samples were introduced into the source by direct gas inlet.

Melting points were taken by a modified Stock procedure.

Reagents. Cyanogen, chlorine, and bromine were obtained from commercial sources and were dried before using. Cesium fluoride, 99.9%, was activated by fusing it in a Pt dish, followed by grinding in a ball mill to a very fine powder under very anhydrous conditions. Potassium fluoride was similarly activated. Manipulation of KF and CsF was done exclusively in the drybox.

Reactions. All reactions except photolysis reactions were carried out in 100-mL glass bulbs fitted with a glass-Teflon valve. In the reaction of (CN)₂ with Br₂/CsF, the reactor was rotated to increase the surface contact of the reactants with CsF. The appropriate metal fluoride was added in the drybox, and the reactor was evacuated. The reactor was then cooled to -196 °C, and the gaseous reactants were condensed into it. The reactor was then warmed to an appropriate temperature and allowed to stand for several hours. The reactor contents were then separated by fractional condensation. The reactions are summarized in Tables I, II, and V. ¹⁹F spectral data for compounds 7 (ClN=CFC-F=NBr), 9 (BrN=CFCF₂NCl₂), 10 (BrN=CFCF₂NClBr), 11 (Cl-N=CFCF₂NClBr), and 12 (ClN=CFCF₂NBr₂), which could only be obtained as a mixture, are listed in Table IV. Characterization of other new compounds follow. The known products 3 (Cl₂NCF₂CF₂NCl₂), 5 (BrN=CFCF=NBr), 6 (ClN=CFCF=NCl), 8 (ClN=CFCF₂NCl₂), and 13 (BrN=CFCF₂NBr₂) were identified by their IR, MS, and ¹⁹F NMR spectra, which agreed with the literature values.[10]

NCCF=NCl (1). NMR: δ -20.4 (s). IR: 2257 (m), 1652 (s), 1641 (s), 1250 (s), 1238 (s), 883 (m), 873 (m), 759 (mw), 652 (mw) cm⁻¹. MS (CI): major m/z 107/109 (MH⁺, 100%), 80/82 (FCNCl⁺), 71 (NCCFN⁺). Mp: -40 °C.

NCCF₂NCl₂ (2). NMR: δ -77.3 (s). IR: 2260 (m), 1199 (vs), 1157 (s), 1105 (vs), 826 (w), 803 (w), 782 (w), 734 (w), 675 (w) cm⁻¹. MS (EI): major m/z 160/162/164 (M⁺, 25%), 134/136/138 (M − CN⁺), 106/108 (M − ClF⁺), 76 (CF₂CN⁺, 100%). Mp: <-82 °C.

NCCF=NBr (4). NMR: δ -4.6 (s). IR: 2256 (m), 1647 (vs), 1228 (s), 1218 (s), 868 (m), 860 (m), 735 (w), 700 (w), cm⁻¹. MS (CI): major m/z 151/153 (MH⁺, 100%), 131/133 (NCCNBr⁺), 106/108 (CNBrH⁺), 93/95 (NBr⁺), 71 (M − Br⁺). Mp: -24 °C.

NCCF₂NClBr (14). NMR: δ -74.1 (s). IR: 2259 (s), 1190 (vs), 1146 (vs), 1105 (vs), 819 (w), 771 (m), 737 (m), 659 (w) cm⁻¹. (Compound 15 was found to be present in a small amount in compound 14 via ¹⁹F NMR and mass spectra; therefore the IR spectrum may contain bands due to compound 15.) MS (CI): major m/z 204/206/208 (M⁺, 100%), 178/180/182 (M − CN⁺), 76 (NCCF₂⁺).

NCCF₂NBr₂ (15). NMR: δ -70.3 (s). MS (CI): major m/z 229/231/233 (M − F⁺, 70%). MS (EI): 248/250/252 (M⁺, 5%). (Compound 15 was not separated from compound 14.)

NCCF=N—N=CFCN (16). NMR: δ -70.4 (s). IR: 2254 (m), 1658 (vs), 1293 (s), 1253 (s), 1149 (w), 1049 (w), 872 (w), 838 (w) cm⁻¹. MS (CI): major m/z 143 (MH⁺, 100%), 86 (NCCFN₂H)⁺, 71 (NCCFN⁺), 53 (C₂N₂H)⁺. MS (EI): 142 (M⁺, 100%), 85 (NCCFN₂⁺), 57 (CFCN⁺), 52 (C₂N₂⁺). Mp: -14 °C.

NCCF₂N=NCF₂CN (17). NMR: δ -80.2 (s). IR: 2262 (m), 1201 (vs), 1101 (s), 1070 (m), 970 (w), 818 (w), 736 (m) cm⁻¹. MS (CI): major m/z 181 (MH⁺, 100%), 152 (M − N₂⁺), 105 (NCCF₂N₂H⁺), 91 (NCCF₂NH⁺), 76 (NCCF₂⁺). Mp: -17 °C.

NCCFN=NCFCN (18). NMR: δ -80.2 (s). IR: 2261 (m), 1231 (m), 1186 (s), 1107 (m), 1068 (w), 969 (w), 901 (w), 733 (w) cm⁻¹. MS (CI): major m/z 143 (MH⁺, 42%), 114 (M − N₂⁺), 95 (M − FN₂), 76 (CFCFN⁺), 69 (NCCFC⁺), 59 (CFN₂⁺), 53 (C₂N₂H⁺, 100%).

NCCF=NC₂F₄Br (19). IR: 2255 (m), 1737 (vs), 1312 (m), 1263 (vs), 1240 (vs), 1106 (vs), 946 (vs), 854 (vs), 812 (m), 767 (m), 739 (w) cm⁻¹. MS (CI): major m/z 251/253 (MH₂, 41%), 231/233 (M − F⁺), 129/131 (CF₂Br⁺), 121 (NCCFNCF₂, 100%)⁺, 100 (NCCFNCF⁺).

NCCF=N(CF₂CCl₂)Br (20). IR: 2283 (m), 1734 (m), 1162 (s), 1026 (w), 1000 (m), 895 (m), 808 (m), 747 (m), 696 (m) cm⁻¹. MS (CI): major m/z 255/257/259/261 (M − CN⁺, 25%), 211/213/215/217 (CF₂CCl₂Br⁺, 100%), 167/169 (CNCF₂CBr⁺).

Results and Discussion

Reactions of (CN)₂ with CsF/Cl₂,Br₂. Representative reactions of cyanogen with Cl₂ and Br₂ in the presence of CsF are summarized in Table I. From these and many other trials, it is apparent that by suitable variation of reactant ratios and conditions, it is possible to carry out selective halofluorination of cyanogen. Chlorine oxidizes the -C≡N bond almost exclusively to the dichloroamine species, whereas bromine stops at the bro-

Table I. CsF-Promoted Reactions of (CN)₂ with Cl₂ and Br₂

mmol of reactants				conditions, °C/h	products (%)[a]
(CN)₂	Br₂	Cl₂	CsF		
1.0		1.2	10	-60/24	NCCF=NCl (1) (trace)
				-60 to -20/48	NCCF₂NCl₂ (2) (19)
2.0		3.0	10	-10 to -5/20	2 (30)
2.0		8.0	35	23/22	2 (24), (CF₂NCl₂)₂ (3) (21)
5.2	10		10	-80 to -20/24	NCCF=NBr (4) (50)
1.5	10		10	23/17	BrN=CFCF=NBr (5) (95)
1.5	1.0	1.0	7	-196 to 23/4	1 (10), 3 (~1), 2 (~1)

[a] Unreacted starting materials were recovered in each case.

Table II. Reactions of NCCF₂NCl₂ with MF/Br₂

reactants (mmol)	conditions, °C/h	products (%)
2 (2.0), Br₂ (4.0), CsF (10)	-196 to 23/5	5, 6, 8,[a] ClN=CFCF=NBr (7), BrN=CFCF₂NCl₂ (9), BrN=CFCF₂NClBr (10), ClN=CFCF₂NClBr (11), ClN=CFCF₂NBr₂ (12)
2 (1.5), Br₂ (10), CsF (19)	-196 to 23/5	BrN=CFCF₂NBr₂ (13) (~80)
2 (1.0), Br₂ (3.0), NaF (4)	0 to 23/20	NCCF₂NClBr (14) (15),[b] NCCF₂NBr₂ (15) (~1)

[a] Essentially 100% conversion to 5-12. Substantial amounts of each were present, but individual yields could not be accurately determined. [b] 2 recovered.

Scheme I. Reaction Paths for (CN)₂ with CsF/X₂
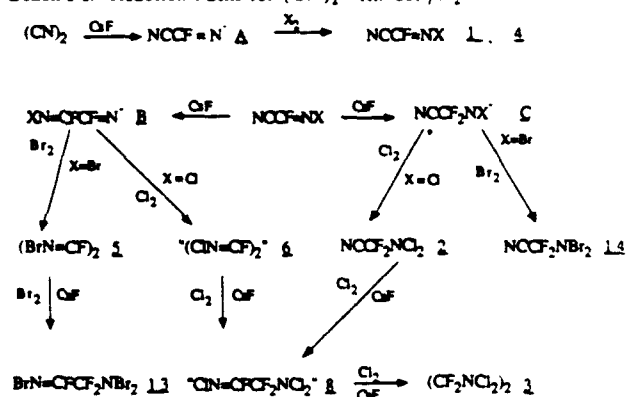
moimine. This is consistent with previous results for a variety of related reactions with R_fCN.[2,3] The observed products can be rationalized by the reaction paths shown in Scheme I. Higher temperatures and excess X₂ clearly favor products 3 and 5. We have no spectroscopic evidence for the proposed anion intermediates A-C, but since the reactions do not occur under the same conditions in the absence of CsF, such intermediates are certainly plausible.[11] Intermediates 6 and 8 are surely formed in these reactions, but under all conditions tried only 2 and 3 could be isolated. Except for 1 and 4, the observed bromine and chlorine products are exclusive. In related work with reactions of (CN)₂ with HgF₂/Cl₂,Br₂, compounds 5, 13, 3(Br), 3, 6, and 8 could be isolated but not 1, 4, 2, and 14.[10]

Reactions of 2 with MF/Br₂. The conversion of N-Cl bonds to N-Br bonds by MF/Br₂ (M = Na, K, Cs) was previously shown to be an effective route to both -NBr₂ and -NClBr derivatives from -NCl₂ compounds.[5,12] We hoped to use this as a means to prepare 11 and 14 as well as the mixed chlorine-bromine derivatives of 8 from compound 2. This turned out to be a complex reaction resulting in a number of interesting new derivatives of cyanogen. Unfortunately, the complex mixture of products resulting from these reactions illustrated in Table II could not be

(11) KF can sometimes be used in place of CsF for reactions of this type, but it was ineffective in promoting the reactions of cyanogen.

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Scheme II. Possible Conversion Paths for $NCCF_2NCl_2$ to $BrN=CFCF_2NBr_2$
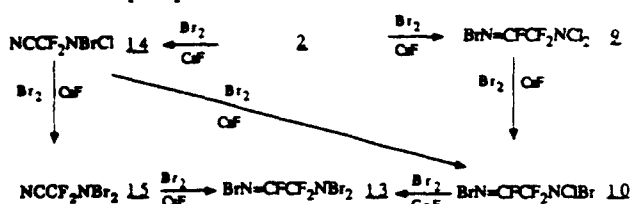
Table III. ^{19}F Chemical Shifts for Representative Chloro and Bromo Amines and Imines[a]

compd	$\delta(CF_3)$	$\delta(CF_2)$	$\delta(CF)$
CF_3NCl_2[14]	-74.1[3]		
CF_3NClBr[5]	-72.3		
CF_3NBr_2[5]	-70.5		
$CF_3CF_2NCl_2$[14]	-78.4	-101.2	
CF_3CF_2NClBr[5]	-77.8	-96.3	
$CF_3CF_2NBr_2$[10]	-77.0	-91.8	
$(CF_2NCl_2)_2$[10]		-92.1	
$(CF_2NBr_2)_2$[10]		-80.2	
$NCCF_2NCl_2$[a]		-77.3	
$NCCF_2NBrCl$[a]		-74.1	
$NCCF_2NBr_2$[a]		-70.3	
$CF_3CF=NCl$[15]	-72.0		-42.1
$CF_3CF=NBr$[10]	-71.6		-26.9
$ClN=CFCF_2NCl_2$[10]		-90.6	-35.7
$BrN=CFCF_2NBr_2$[10]		-81.0	-19.9
$NCCF=NCl$[a]			-20.4
$NCCF=NBr$[a]			-4.6
$(CF=NCl)_2$[10]			-37.1
$(CF=NBr)_2$[10]			-20.1

[a]This work.

Table IV. ^{19}NMR: Mixed Fluoro–Chloro/Bromo Derivatives of $(CN)_2$

compd	$\delta(CF)$	$\delta(CF_2)$	$^3J_{FF}$, Hz
$ClN=CF^ACF^B=NBr$ (7)	-20.2 (B, d), -35.2 (A, d)[a]		11.6
$BrN=CFCF_2NCl_2$ (9)	~-20.7 (t)[b]	-90.2 (d)	7.3
$BrN=CFCF_2NClBr$ (10)	~-20.7 (t)[b]	-85.8 (d)	7.3
$ClN=CFCF_2NClBr$ (11)	~-35.1 (t)[b]	-86.5 (d)	7.3
$ClN=CFCF_2NBr_2$ (12)	~-35.1 (t)[b]	-82.3 (d)	7.3

[a]Overlaps with 11 and 12 but doublet clearly present. [b]Overlapping, but two triplets are evident.

Table V. Photolysis of Compounds 2, 4, and 14

compd (mmol)	conditions. mL/h[a]	products (%)[b]
$NCCF=NBr$ (4) (2.0)	250/96	$NCCF=N-N=CFCN$ (16) (80), Br_2
$NCCF=NBr$ (4) (2.0)	15/200	16 (10), Br_2
$NCCF_2NClBr$ (14) (0.5)	100/1	$NCCF_2N=NCF_2CN$ (17) (20), $BrCl$
$NCCF_2NCl_2$ (2) (1.0)	15/3	17 (5), $NCCF_2Cl$, Cl_2
$NCCF_2NCl_2$ (2) (1.0)	500/3	17 (50), Cl_2

[a]Direct South Carolina sunlight. [b]Balance of starting material was converted to nonvolatile residue.

Table III contains a summary of relevant compounds, and the regular shift of the fluorine signals to lower field in going from chlorine to bromine is clearly apparent.

With the aid of the data in Table III and mass spectrometry, good support for the structures of the new compounds 7 and 9–12 was obtained for a mixture of 5–12. The mass spectrum of the mixture gave fairly intense molecular ions for $C_2N_2F_3ClBr_2$, $C_2N_2F_3BrCl_2$, and $C_2N_2F_2BrCl$ with the appropriate isotopic ratios as well as peaks that could be assigned to molecular ions of 5, 6, and 8. Of course this cannot distinguish 9 from 11 or 10 from 12 but is very supportive when combined with the NMR data. The ^{19}F NMR data for 7 and 9–12 present in the mixture of 5–12 are summarized in Table IV. The overlapping peaks in the XN=CF– region for 9–12 make assignment of accurate chemical shifts difficult, but the remainder of the spectra are well resolved.

Several of the reported new compounds 1, 2, 4, 7, and 9–11 could exist either as E or Z isomers or as a mixture of both isomers. From the available data, it is certain that 1, 2, and 4 are formed as a single isomer. The value of $\delta(CF)$ suggests that the observed isomer is Z in each case, and this has been confirmed for 4 by microwave spectroscopy.[16] On the basis of minimizing steric interactions, it is likely that 7 is Z,Z and that 9–11 are also the Z isomers. Compounds 11, 14, and 10 contain a chiral nitrogen atom, and the adjacent methylene fluorines are diastereotopic in related compounds in which one of the halogens on nitrogen is fluorine.[2] However, in agreement with other –NClBr derivatives, the nitrogen inversion is fast at near room temperature and first-order spectra are observed.[5]

Selected Reactions of 2, 4, and 14. All the N-halogen derivatives reported in this work appear to have reasonable thermal stability and are stable at 23 °C in glass in the absence of moisture and light. Pyrex-filtered sunlight is sufficiently energetic to cause rapid photolysis of the N-bromo derivatives and much less so for the N-chloro species. Previously, we and others have shown that photolysis or thermolysis often leads to an efficient coupling through nitrogen in both –CF=N–Br and –NBr₂ and –NCl₂ derivatives.[3,5,17] We investigated the photolysis of 2, 4, and 14 by Pyrex-filtered sunlight to see if the respective azines and azo

separated and, in general, conditions could not be found to favor a particular product except for 13. Thus 7 and 9–12 were only identified in a mixture.

For the formation of 13 the reaction can be explained as shown in Scheme II. The high conversion to 13 is driven by the large excess of Br_2. When only a 2 to 1 excess of Br_2 to 2 is employed, one observes the complex mixture of products 5–12, which contains the intermediates 9 and 10 of Scheme II. The products 8–12 can be explained by the conversion of –NCl₂ to NBrCl and –NBr₂ by the mixture of Br_2, $BrCl$, and Cl_2 that is present after the reaction begins.[13] As illustrated in Table I, $BrCl$ (starting with a 1:1 mixture of Cl_2 to Br_2) converts –CN to –CF=NCl and is apparently less reactive than Cl_2 or Br_2 alone. The presence of 5–7, however, is not readily explained. The most likely route to these compounds is through an elimination under the reaction conditions of XF from 7–13 or from 2, 14, or 15, followed by oxidation of –C≡N to –CF=NX. However, in the absence of MF/X₂, all the compounds appear to be stable at 23 °C. Clearly, this is a complex reaction and highly dependent on the reaction conditions. It was somewhat fortuitous that 5–12 were observed in a single reaction.

Finally, the reaction of 2 with NaF/Br_2 is of interest since it clearly shows that NaF is effective in converting N—Cl to N—Br bonds by bromine but ineffective in promoting the oxidation of –C≡N. Both of these points were expected from previous results.[5,9]

Characterization of Halogen Derivatives of $(CN)_2$. Data for new compounds 1, 2, 4, 14, and 15 are contained in the Experimental Section. For those compounds that could be isolated in essentially pure form, the combination of IR, MS, and ^{19}F NMR spectra provides good proof of structure. The ^{19}F NMR spectra of these and related compounds show a remarkably regular variation in chemical shifts as a function of the halogens chlorine and bromine, and this can be used effectively to distinguish CF_3NX_2, $-CF_2NX_2$, and $-CF=NX$, for X = Cl, Br.

(13) BrCl is in equilibrium with Br_2 and Cl_2 at 25 °C: Mathau, H. C.; Pachuki, C. F.; Hawkins, N. J. *J. Chem. Phys.* **1954**, *22*, 1117.

(14) Hvnes, J. B.; Austin, T. E. *Inorg. Chem.* **1966**, *5*, 488.

(15) This compound was first prepared by: Chambers, W. J.; Tullock, C. W.; Coffman, D. D. *J. Am. Chem. Soc.* **1962**, *84*, 2337. It was later prepared by an alternative route: Sekiya, A.; DesMarteau, D. D. *J. Org. Chem.* **1981**, *46*, 1277. The NMR of $CF_3CF=NCl$ was not reported in either of these references but was determined by the latter authors as $\delta(CF_3)$ -72.0, $\delta(CF)$ -42.1, J_{FF} = 5.2 Hz.

(16) DesMarteau, D. D.; Groner, P.; Nanaie, H.; Durig, J. R. To be published.

(17) Bauknight, C. W.; DesMarteau, D. D. *J. Org. Chem.* **1988**, *53*, 443.

Scheme III. Fluoride-Catalyzed Cyclization of the Azine 16
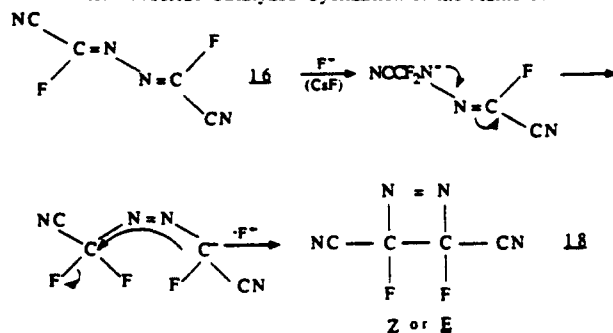
compounds could be isolated. The results are summarized in Table V. High pressure decreased the yields of coupled products and led to greater formation of nonvolatile liquid and solid residues (presumably polymeric).

Both **16** and **17** were readily identified by their simple but indicative IR and NMR spectra and large parent ions in their mass spectra. The chemical shifts are reasonable for compounds of this structure, and the single resonance for each indicates only one of two possible geometric isomers is formed in each case, presumably Z,Z for **16** and E for **17**.[18]

Compound **16** is an unusual example of a conjugated system of double and triple C—N bonds. When **16** was condensed onto CsF at -196 °C and warmed to 22 °C, it underwent a rapid reaction (90% of **16** was absorbed by the CsF turning the CsF red-brown) with loss of the $\sqrt{C}$=N at 1658 cm^{-1} in the IR spectra of the volatile product and a shift in the single fluorine resonance from -70.4 to -80.2 ppm. The mass spectrum exhibits a large parent ion in the CI at m/z 143 (MH$^+$) identical with that of **16**, but the fragmentation pattern is much different. We explain this result on the basis of a fluoride-catalyzed cyclization of **16** to **18**, as shown in Scheme III.[19,20] **18** can exist as the E or Z isomer.

(18) See refs 3 and 9. See also: Perfluorohalogeno-Organo Compounds. *Gmelins Handbuch der Anorganische Chemie*, 8th ed.; Springer Verlag: West Berlin. 1980; Part 8.
(19) The internal nucleophilic displacement of fluoride ion from a saturated carbon is unusual, but precedent for such reactions in cyclizations exists: Chambers, R. D.; Lindley, A. A.; Philpot, P. D.; Fielding, H. C.; Hutchison, J.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 214.
(20) The related compound CF$_2$=N—N=CF$_2$ also reacts rapidly with CsF to give a brown oil and solid which has not been characterized (Ogden, P. H. *J. Chem. Soc. C* **1971**, 2920). The known cyclic compound CF$_2$N=NCF$_2$ is apparently not formed in the latter reaction but is readily prepared from (CN)$_2$ and AgF$_2$ which might be mechanistically similar to the formation of **18** from **16** (Emeleus, H. J.; Hurst, G. L. *J. Chem. Soc.* **1962**, 3021).

Both isomers should exhibit only a single resonance in the ^{19}F NMR spectrum, and the presence of only one signal in the observed spectrum indicates that only one of the possible isomers is present. However, the configuration cannot be determined from the available data.

Finally, *reactions of 4 with alkenes* were carried out to see if this compound would undergo addition reactions as observed for other bromoimines.[3,17] Thermal reactions were carried out with C$_2$H$_4$, C$_2$F$_4$, and CF$_2$CCl$_2$ by combining equimolar amounts of the reactants in a 100-mL glass reactor in the dark at 80 °C. This procedure gave only traces of molecular adducts, and decomposition and polymer oils were the main products. At 22-25 °C the results were the same for C$_2$H$_4$ after 1 day, but C$_2$F$_4$ and CF$_2$CCl$_2$ showed small amounts of the adducts after 11 and 24 days, respectively.

$$4 + C_2H_4 \rightarrow \text{oil, SiF}_4$$

$$4 + C_2F_4 \rightarrow NCCF=NCF_2CF_2Br \ (19) + \text{other} \ (\sim 5\%)$$

$$4 + CF_2CCl_2 \rightarrow NCCF=N(CF_2CCl_2)Br \ (20) + \text{other} \ (\sim 4\%)$$
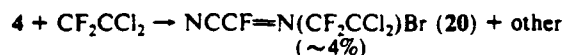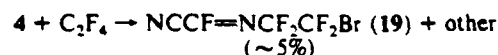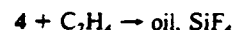
These products were only identified by IR spectroscopy and MS, and the regioisomer formed in the case of CF$_2$CCl$_2$ was not determined. The low yields of these additions compared to previous work with CF$_2$=NX (Cl, Br) and R$_f$CF=NBr reactions with a variety of alkenes must be due in part to the inherent tendency of **4** to polymerize under radical conditions, as shown by the photolysis of **4**.

Summary

The selective bromo- and chlorofluorination of cyanogen using CsF/Cl$_2$Br$_2$ has been demonstrated. Bromine forms only the bromoimines, whereas Cl$_2$ yields predominantly the dichloroamines. By selective control of reaction conditions, the stepwise oxidation of CN groups in cyanogen can be achieved. The substitution of Cl by Br and/or the bromofluorination of NCCF$_2$NCl$_2$ is a complex reaction resulting in 11 identifiable structural isomers of the possible bromo- and chlorofluorination products of cyanogen. Photolysis reactions of selected haloimine and haloamine derivatives of cyanogen provide routes to novel azines and azo compounds which are C-fluorinated derivatives of the dimer of cyanogen.

Halogen exchange reactions of perhalo-3-azaalkenes and their subsequent dehalogenation to form hetero-1,3-dienes

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Abstract

Treatment of the perhalogenated azaalkenes, $R_xCF=NCF_2CFXBr$ ($R_x = CF_3$, C_2F_5, $ClCF_2$; $X = F$, CF_3) with $AlCl_3$ readily produces new imines of the type $R_xCCl=NCCl_2CFXBr$ and $R_xCCl_2N=CClCFXBr$. Dehalogenation of these new imines using activated zinc dust affords a series of novel hetero-1,3-dienes ($R_xCCl=NCCl=CFX$).

Introduction

Studies of the reaction chemistry of N-bromoperhalo-1-alkanimines ($R_xCF=NBr$) have so far shown that they react quite readily under thermal conditions with halogenated olefins to form 1,2-addition products [1]. The addition to a majority of unsymmetrical olefins was found to be highly regioselective, where during the addition the $R_xCF=N-$ group adds preferentially to the end of the olefin which would result in the formation of the most stable radical. As a result the reaction between $R_xCF=NBr$ and $CF_2=CFX$ affords perhalo-3-azaalkenes of the structure shown in eqn. (1).

$$\underset{F}{\overset{R_x}{\diagdown}}C=NBr + CF_2=CFX \xrightarrow{\;\Delta\;} \underset{F}{\overset{R_x}{\diagdown}}C=NCF_2CFXBr \qquad (1)$$

$R_x = CF_3$, C_2F_5, $ClCF_2$; $X = Br$, Cl, F, CF_3

Recently our studies have concentrated on the reaction chemistry of the perhalo-3-azaalkenes and, in particular, their use as synthetic intermediates in the preparation of hetero-1,3-dienes.

Novel 1,3-dienes of the type $R_xC(O)N=CFCF_2Br$ can easily be prepared by hydrolysis of the perhalo-azaalkenes, followed by dehydrofluorination of perhaloacidamides, $R_xC(O)N(H)CF_2CF_2Br$, with KF [2].

We now report the synthesis of another series of hetero-1,3-dienes having the structure $R_xCCl=NCCl=CFX$.

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2

Experimental

General methods

All work was carried out in a Pyrex vacuum system equipped with glass–Teflon valves. Pressures were measured with a Wallace Tiernan series 1500 differential pressure gauge. Quantities of reactants and products were measured by direct weighing or by PVT measurements. Temperatures were measured by using a digital-indicating iron–constantan thermocouple.

Infrared spectra were recorded using a Perkin–Elmer 1430 spectrometer with a Model 3600 data station, using a 10-cm glass cell fitted with KCl windows. NMR spectra were recorded using a JEOL FX-90Q spectrometer using various deuterated media as both solvent and internal lock, and ~1% $CFCl_3$ as the internal reference. Chemical shifts are negative upfield from $CFCl_3$. Mass spectra were recorded using a Hewlett–Packard 5985B instrument at 70 eV for electron-impact (EI) and chemical ionization [(CI), CH_4)] spectra. Samples were introduced by direct gas injection.

Boiling points were determined using Siwoloboff's method [11] and are uncorrected.

Reagents

Aluminum chloride ($AlCl_3$) and zinc dust were obtained from commercial sources; $AlCl_3$ was freshly sublimed before use and zinc dust was activated by treatment with 2 N HCl, followed by washing with H_2O and then dried in vacuo. The compounds $CF_3CF=NCF_2CF_2Br$, $C_2F_5CF=NCF_2Br$, Cl-$CF_2CF=NCF_2CF_2Br$ and $CF_3CF=NCF_2CFBrCF_3$ were prepared using methods reported earlier [1].

General procedure for the reaction between $R_xCF=NCF_2CFXBr$ and $AlCl_3$

The imine (2–4 mmol) was condensed onto a five-fold excess of freshly sublimed $AlCl_3$ cooled to -196 °C in a 140 ml glass reactor. The flask was warmed to room temperature and the mixture magnetically stirred for a period of ~16 h. The volatiles were then pumped off from the solid and collected in a -196 °C trap. Purification was carried out by a series of trap-to-trap distillations to afford the product in 65–70% yield. Characterizations of the new imines are described below.

$CF_3CCl=NCCl_2CF_2Br$ and $CF_3CCl_2N=CClCF_2Br$

(2:3 mixture), glass at -90 °C to -88 °C. IR (gas): 1698 (vs) (C=N), 1283 (vs), 1228 (vs), 1185 (vs), 1065 (vs), 1021 (vs), 954 (m), 929 (s), 865 (vs), 838 (w), 803 (w), 774 (s), 673 (w), 609 (m) cm^{-1}. MS: (CI, major m/z): 346/344/342 [(M+1)$^+$], 310/308/306 [(M−Cl)$^+$, 100%], 216/214/212 [(M−CF_2Br)$^+$], 215/213/211 (CCl_2CF_2Br), 155/153/151 (CF_3CCl_2$^+$). (EI, major m/z): 310/308/306 [(M−Cl)$^+$], 276/274/272 [(M−CF_3)$^+$], 216/214/212 [(M−CF_2Br)$^+$], 155/153/151 (CF_3CCl_2$^+$), 69 (CF_3$^+$, 100%). ^{19}F NMR (C_6D_6): $CF_2^ACCl=NCCl_2CF_2^BBr$, δA -72.6, δB -62.2; $CF_3^CCCl_2N=CClCF_2^DBr$, δC -83.0, δD -56.8; $J_{AB}=J_{CD}=0$ Hz.

CF₃CF₂CCl=NCCl₂CF₂Br and CF₃CF₂CCl₂N=CClCF₂Br

$CF_3CF_2CCl\!=\!NCCl_2CF_2Br$ and $CF_3CF_2CCl_2N\!=\!CClCF_2Br$

(10:1 mixture), glass flowing at slowly -76 °C to -74 °C, vap. press. ~ 1.5 Torr at 25 °C. IR (liquid film): 1690 (vs) (C=N), 1345 (s), 1329 (s), 1228 (vs), 1209 (vs), 1185 (s), 1160 (vs), 1081 (s), 1067 (s), 1007 (vs), 987 (s), 874 (s), 767 (s), 744 (m), 695 (w), 656 (w) cm⁻¹. MS (CI, major m/z): 396/394/392 [(M + 1)⁺], 306/358/356 [(M − Cl)⁺, 100%], 266/264/262 [(M − CF₂Br)⁺], 215/213/211 (CCl₂CF₂Br⁺), 205/203/201 (C₂F₅CCl₂⁺), 131/129 (CF₂Br⁺), 119 (C₂F₅⁺). (EI, major m/z): 360/358/356 [(M − Cl)⁺], 266/264/262 [(M − CF₂Br)⁺], 69 (CF₃⁺, 100%). ¹⁹F NMR (C₆D₆): $CF_3{}^ACF_2{}^BCCl\!=\!NCCl_2CF_2{}^CBr$, δA -81.4, δB -114.4, δC -62.4; $CF_3{}^DCF_2{}^ECCl_2N\!=\!CClCF_2{}^FBr$, δD -75.8, δE -120.6, δF -56.8; all j values ≈ 0 Hz.

ClCF₂CCl=NCCl₂CF₂Br and ClCF₂CCl₂N≡CClCF₂Br

$ClCF_2CCl\!=\!NCCl_2CF_2Br$ and $ClCF_2CCl_2N\!\equiv\!CClCF_2Br$

(1:1 mixture), glass flowing slowly at -86 °C to -84 °C, vap. press. ~ 1 Torr at 25 °C. IR (liquid film): 1688 (s) (C=N), 1275 (w), 1225 (vs), 1163 (s), 1170 (vs), 1029 (s), 1000 (vs), 863 (s), 793 (vs), 764 (vs), 688 (m), 665 (w), 640 (m), 606 (m) cm⁻¹. MS (CI, major m/z): 326/342/332 [(M − Cl)⁺, 100%], 276/274/272 [(M − CF₂Cl)⁺], 232/230/228 [(M − CF₂Br)⁺], 213/211 (CCl₂CF₂Br⁺), 171/169/167 (CCl₂CF₂CCl⁺). (EI, major m/z): 131/129 (CF₂Br⁺), 99/97 (CF₂CCl⁺), 87/85 (CF₂Cl⁺). ¹⁹F NMR (C₆D₆): $ClCF_2{}^ACClNCCl_2CF_2{}^BBr$, δA -59.7, δB -62.1; $ClCF_2{}^CCCl_2N\!=\!CClCF_2{}^DBr$, δC -67.5, δD -56.5; $J_{AB}\!=\!J_{CD}\!=\!0$ Hz.

CF₃CCl₂N=CClCFBrCF₃

$CF_3CCl_2N\!=\!CClCFBrCF_3$

Glass flowing slowly at -81 °C to -79 °C. IR (liquid film): 1691 (vs) (C=N), 1278 (vs), 1209 (vs), 1166 (s), 1089 (m), 1057 (s), 932 (s), 903 (vs), 852 (s), 813 (m), 739 (w), 719 (m), 647 (w) cm⁻¹. MS (EI, major m/z): 360/358/356 [(M − Cl)⁺ 100%], 326/324/322 [(M − CF₃)⁺], 279/277 [(M − BrCl)⁺], 181/179 (CF₃CFBr⁺), 155/153/151 (CF₃CCl₂⁺), 69 (CF₃⁺). ¹⁹F NMR (C₆D₆): $CF_3{}^ACCl^2N\!=\!CClCF^BBrCF_3{}^C$, δA -83.3, σB -127.3 (q), δC -76.3 (d); $j_{BC}\!=\!8.8$ Hz.

General procedure for the dehalogenation of $R_xCCl\!=\!NCCl_2CFXBr$ and $R_xCCl_2N\!=\!CClCFXBr$

The isomeric mixture of the imine (3.0 mmol) was condensed onto a mixture of activated zinc dust (1.0 g) and sulfolane (5.0 ml), and cooled to -196 °C whilst contained in a 140 ml glass reactor. After warming to room temperature, the contents of the vessel were magnetically stirred for ~ 1 h and the volatiles were then pumped off and collected in a -196 °C trap. Purification was achieved by vacuum-line fractionation to give the corresponding hetero-1,3-dienes ($R_xCCl\!=\!NCCl\!=\!CFX$) in approximately 80% yield. The compounds were characterized as described below.

CF₃CCl=NCCl=CF₂

$CF_3CCl\!=\!NCCl\!=\!CF_2$

Boiling point, 89.5 °C. IR (gas): 1708 (vs) (C=N), 1668 (w) (C=C), 1343 (vs), 1291 (vs), 1233 (vs), 1180 (vs), 1030 (vs), 946 (s), 760 (s),

737 (w) cm^{-1}. MS (CI, major m/z): 232/230/228 [(M+1)$^+$], 231/229/227 [M$^+$], 210/208 [(M−F)$^+$], 194/192 [(M−Cl)$^+$, 100%], 160/158 [(M−CF$_3$)$^+$]. (EI, major m/z): 231/229/227 [M$^+$], 210/208 [(M−F)$^+$], 194/192 [(M−Cl)$^+$, 100%], 118/116 (CF$_3$CCl$^+$), 99/97 (CF$_2$CCl$^+$). ^{19}F NMR (C$_6$D$_6$): CF$_3$^{A}CCl=NCCl=CF^{B}F^C, δA −71.9, δB −72.8 (d), δC −82.3 (d); j_{BC}=22 Hz, Δδ$_{BC}$=797 Hz. Mol. wt.: calcd 227.9, found 228.6.

$CF_3CF_2CCl=NCCl=CF_2$
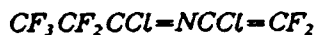
Boiling point, 111 °C. IR (gas): 1704 (vs) (C=N), 1664 (m) (C=C), 1344 (vs), 1290 (w), 1219 (vs), 1157 (s), 1073 (s), 1028 (vs), 884 (s), 853 (vs), 750 (s), 721 (s), 670 (w) cm^{-1}. MS (CI, major m/z): 281/279/277 [M$^+$, 100%], 262/260/258 [(M−F)$^+$], 244/242 [(M−Cl)$^+$], 162/160/158 [(M−C$_2$F$_5$)$^+$]. (EI, major m/z): 281/279/277 [M$^+$], 244/242 [(M−Cl)$^+$], 119 (C$_2$F$_5$$^+$), 99/97 (CF$_2Cl^+$), 69 (CF$_3$$^+$, 100%). ^{19}F NMR (C$_6D_6$): CF$_3^{A}CF_2$^{B}CCl=NCCl=CF^{C}F^D, δA −81.5, δB −113.9, δC −72.2 (d), δD −8.1.5 (d); J_{CD}=24.9 Hz, Δδ$_{CD}$=784 Hz. Mol. wt.: calcd. 277.9, found 279.3.

$ClCF_2CCl=NCCl=CF_2$
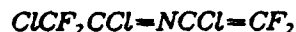
Boiling point, 115–117 °C. IR (gas): 1707 (vs) (C=N), 1669 (w) (C=C), 1341 (vs), 1292 (w), 1237 (vs), 1187 (s), 1155 (s), 1130 (w), 1098 (w), 1035 (vs), 957 (w), 865 (s), 826 (m), 796 (w), 716 (m), 644 (w) cm^{-1}. MS (CI, major m/z): 248/246/244 [(M+1)$^+$], 228/226/224 [(M−F)$^+$], 210/208 [(M−Cl)$^+$, 100%], 168/158 [(M−CF$_2$Cl)$^+$]. (EI, major m/z): 247/245/243 [M$^+$], 210/208 [(M−Cl)$^+$], 160/158 [(M−CF$_2$Cl)$^+$, 100%], 99/97 (CF$_2$CCl$^+$), 87/85 (CF$_2$Cl$^+$). ^{19}F NMR (C$_6$D$_6$): ClCF$_2$^{A}CCl=NCCl=CF^{B}F^C, δA −57.9, δB −73.2 (d), δC −82.5 (d); j_{BC}=22.0 Hz, Δδ$_{BC}$=785 Hz. Mol. wt.: calcd 244.5, found 247.3.

$CF_3CCl=NCCl=CFCF_3$

(Mixture of E and Z isomers, ratio ~1:9), b.p., 109.5 °C. IR (gas): 1703 (s) (C=N), 1669 (s) (C=C), 1353 (vs), 1288 (vs), 1235 (vs), 1220 (vs), 1188 (vs), 1174 (vs), 1132 (m), 1096 (m), 1061 (w), 970 (vs), 906 (w), 874 (s), 822 (w), 763 (s), 724 (vs), 648 (s) cm^{-1}. MS (CI, major m/z): 281/279/277 [M$^+$, 100%], 262/260/258 [(M−F)$^+$, 244/242 [(M−Cl)$^+$, 210/208 [(M−CF$_3$)$^+$]. (EI, major m/z): 281/279/277 [M$^+$], 210/208 [(M−CF$_3$)$^+$], 149/147 (CF$_3$CFCCl$^+$), 69 (CF$_3$$^+$). ^{19}F NMR (C$_6D_6$): Z-CF$_3$^{A}CCl=NCCl=CF^{B}CF$_3$^{C}, δA −72.4, δB −123.2 (q), δC −66.1 (d); J_{BC}=9.4 Hz; E-CF$_3$^{D}CCl=NCCl=CF^{E}CF$_3$^{F}, δD −71.0, δE −127.0 (q), δF −64.9 (d); J_{EF}=8.8 Hz.

Results and discussion

Halogen exchange reaction

The fact that the addition reactions of N-bromoimines to unsymmetrical olefins is highly regioselective creates a problem in trying to use these

perhalo-azaalkenes as precursors to hetero-1,3-dienes. Ideally one would like the reverse addition to take place as this would give rise to compounds of the type $R_xCF=NCFXCF_2Br$, where $X=Br$, Cl. A 1,2-dehalogenation could then be achieved by a variety of methods to afford the desired perhalogenated dienes, $R_xCF=NCF=CF_2$. Unfortunately this is not the case, since the addition always occurs in such a manner that the heaviest halogens are attached to the same terminal carbon. Alternatively, the reaction of N-bromoimines with symmetrical halogenated olefins $XCF=CFX$ other than $CF_2=CF_2$ was unsuccessful and no addition products were observed. As a result, formation of perhalo-3-azaalkenes containing a halogen other than fluorine on the carbon adjacent nitrogen via these routes had to be abandoned.

α,α,α'-Trichloro(perfluoro)azaalkenes that contain all three chlorine atoms centered around the imine group ($CCl=NCCl_2^-$) have been prepared previously by treating the corresponding perfluorinated tertiary amine with $AlCl_3$ [3–5]. In most cases the reaction gives rise to an isomeric mixture (eqn. (2)):

$$(CF_3CF_2)_2NCF_2R_f \xrightarrow{AlCl_3} CF_3CCl=NCCl_2R_f + CF_3CCl_2N=CClR_f \qquad (2)$$

The reaction is believed to proceed via the intermediate perfluoroazaalkene $CF_3CF=NCF_2R_f$, which in the presence of $AlCl_3$ undergoes a series of halogen-exchange reactions to give the observed products. The perhalo-azaalkenes used in our study all have the basic structure $R_xCF=NCF_2CFXBr$ ($R_x=CF_3$, C_2F_5, $ClCF_2$, $X=F$ or CF_3), and each of these compounds contains three fluorine atoms centered around the imine group. We therefore decided to use this procedure to see if similar trichloro-azaalkenes to those already reported could be prepared.

The reaction conditions employed were rather mild: the alkanimines were stirred with an excess of dry $AlCl_3$ at room temperature for a period of approximately 16 h and the products formed were identified as those given in Table 1. In all cases the three fluorine atoms centered around the imine functionality were exchanged by chlorine and in all but one example ($R_x=CF_3$, $X=CF_3$) a mixture of isomeric imines were formed. The ratio of each isomer was determined from their ^{19}F NMR spectra.

Previous work has shown that $AlCl_3$ can readily be used for replacing fluorine by chlorine. Perfluorocyclic ethers of the type shown below can easily be converted to their α,α,α'-trichloro analogs with $AlCl_3$ [6] [eqn. (3)]:

TABLE 1

Reaction of $R_xCF=NCF_2CFXBr$ with $AlCl_3$

Azaalkene	Products (isomer ratio)
$CF_3CF=NCF_2CF_2Br$	$CF_3CCl_2N=CClCF_2Br$, $CF_3CCl=NCCl_2CF_2Br$ (3:2)
$C_2F_5CF=NCF_2CF_2Br$	$C_2F_5CCl_2N=CClCF_2Br$, $C_2F_5CCl=NCCl_2CF_2Br$ (1:10)
$ClCF_2CF=NCF_2CF_2Br$	$ClCF_2CCl_2N=CClCF_2Br$, $ClCF_2CCl=NCCl_2CF_2Br$ (1:1)
$CF_3CF=NCF_2CFBrCF_3$	$CF_3CCl_2N=CClCFBrCF_3$ (one isomer)

$$R_f\overset{\displaystyle CF(CF_2)_nCF_2}{\underset{O}{\rule{0pt}{0pt}}} \xrightarrow{AlCl_3} R_f\overset{\displaystyle CCl(CF_2)_nCCl_2}{\underset{O}{\rule{0pt}{0pt}}} \tag{3}$$

The mechanism proposed for this conversion involves the formation of an aluminum complex by the abstraction of an α-fluorine, *i.e.*

$$\overset{\displaystyle }{\underset{\displaystyle }{}} CF\text{-}O\text{-}CF_2 \xrightarrow{AlCl_3} [\, CF\text{-}O\text{-}CF^+ \longleftrightarrow CF\text{-}O\!\!=\!\!CF\,]\ AlCl_3F^-$$

Exchange is then completed by abstracting a chloride ion from $AlCl_3F^-$ by the carbocation intermediate. The process is repeated a further two times until the trichloro derivative is finally formed.

In an attempt to obtain more information with regard to the mechanism of the halogen exchange, a series of reactions were carried out on the 3-azaalkene, $CF_3CF\!\!=\!\!NCF_2CF_2Br$, using varying quantities of $AlCl_3$. Our results showed that before halogen exchange occurs, the imine undergoes isomerization [eqn. (4)] similar to the equilibrium that has also been observed when the imine is treated with active KF.

$$CF_3CF\!\!=\!\!NCF_2CF_2Br \xrightleftharpoons{AlCl_3} CF_3CF_2N\!\!=\!\!CFCF_2Br \tag{4}$$

The next step is probably similar to that already described, in that an anionic aluminum complex is formed by the abstraction of the α'-fluorine ($CF\!\!=\!\!N$) from each of the isomeric imines. This will then give rise to the carbonionic intermediates shown in Scheme 1.

Chlorination then occurs to afford the two monochloro-imines (A) and (A'). A mixture of these isomers (1A:3A') was successfully isolated in a 3:1 reaction of $CF_3CF\!\!=\!\!NCF_2CF_2CF_2Br$ with $AlCl_3$ and identified by ^{19}F NMR spectroscopy [$CF_3^ACCl\!\!=\!\!NCF_2^BCF_2^CBr$, δA -73.2 (s), δB -99.8 (t), δC -69.0 (t); $J_{BC}=6.0$ Hz; $CF_3^ACF_2^BN\!\!=\!\!CClCF_2^CBr$, δA -86.0 (s), δB -103.2 (s), δC -57.4 (s)].

The next step would entail the removal of an α-fluorine from the $N\!\!-\!\!CF_2$ group of each of the two isomers. This then gives rise to a series of resonance-stabilized intermediates shown in Scheme 2.

$CF_3CF = NCF_2CF_2Br \xrightleftharpoons{AlCl_3} CF_3CF_2N = CFCF_2Br$

$AlCl_3 \downarrow -F^-$ $AlCl_3 \downarrow -F^-$

$\overset{(+)}{CF_3C = NCF_2CF_2Br}$ $\overset{(+)}{CF_3CF_2N = C\text{-}CF_2Br}$

$AlCl_3F^- \downarrow +Cl^-$ $AlCl_3F^- \downarrow +Cl^-$

$CF_3CCl = NCF_2CF_2Br$ $CF_3CF_2N = CClCF_2Br$

(A)   (A')

Scheme 1.

$CF_3CCl = NCF_2CF_2Br$ $\qquad\qquad$ $CF_3CF_2N = CClCF_2Br$

$\cdot F^-\Big\downarrow$ $\qquad\qquad\qquad\qquad$ $\cdot F^-\Big\downarrow$

$CF_3CCl = \overset{(+)}{N}CFCF_2Br$ (a) $\qquad$ $CF_3\overset{(+)}{C}FN = CClCF_2Br$ (a')

$\Big\updownarrow$ $\qquad\qquad\qquad\qquad\qquad$ $\Big\updownarrow$

$CF_3\overset{(+)}{C}ClN = CFCF_2Br$ (b) $\qquad$ $CF_3CF = \overset{(+)}{N}CClCF_2Br$ (b')

$\Big\downarrow +Cl^-$ $\qquad\qquad\qquad\qquad$ $\Big\downarrow +Cl^-$

$CF_3CCl = NCFClCF_2Br$ $\qquad\qquad$ $CF_3CFClN = CClCF_2Br$

(B) $\qquad\qquad\qquad\qquad\qquad$ (B')

Scheme 2.

The canonical forms (a, a') and (b, b') are also further stabilized by the effect of a mesomeric interaction which occurs between an empty orbital on carbon and an unshared pair of electrons on the adjacent halogen

$-\overset{|}{\underset{|}{C}}-\ddot{Y} \longleftrightarrow -\overset{|}{\underset{|}{C}}=\overset{+}{Y}$ (Y = F, Cl)

The (+M) effect of the fluorine is stronger than that of chlorine [7], thus fluorine should bestow a greater degree of stability on the canonical forms (a) and (a'). This is also coupled with the fact that chlorine has a greater stabilizing effect on the imine (C=N) bond than does fluorine. Therefore if we consider these intermediates to be the predominant ones. The addition of chloride ion will afford the dichloro-compounds (B) and (B'). Unfortunately all attempts at isolating the dichloro derivatives have so far proved unsuccessful. The process is further repeated until the α,α,α'-trichloro analogs are finally formed.

The ratio of the isomers formed cannot be easily explained. It may arise from the initial step of isomerisation of the unreacted imine, although we have no clear evidence that the ratio of the final products is related to the ratio of the unreacted imine isomers. We could base our observations on steric grounds. After abstraction of the third fluorine the following stabilized cation is formed:

$R_x\overset{(+)}{C}Cl\text{-}N = CClR_y \longleftrightarrow R_xCCl = N\text{-}\overset{(+)}{C}ClR_y$

$R_x = CF_3$, C_2F_5, $ClCF_2$, $R_y = CF_2Br$, $-CFBrCF_3$

In the case where $R_x = ClCF_2$ and $R_y = BrCF_2$, these two groups are of similar size; hence Cl^- should show an equal preference to attach at either carbon adjacent to the two groups. As a result we would expect the products to be a 1:1 mixture of isomers, which is in agreement with the result observed.

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When $R_x = CF_3$, $R_y = CFBrCF_3$, R_y is bulkier than R_x, thus on steric grounds we would expect Cl^- to attach preferentially at the position adjacent the group R_x. This would give rise to $CF_3CCl^2N=CClCFBrCF_3$ as the major isomeric product. In this case the steric effect must be extremely predominant as no trace of the other isomer $CF_3CCl=NCCl_2CFBrCF_3$ was detected.

The identity of the new compounds is strongly supported by the data given in the experimental section. In most cases, molecular ions MH^+ are observed and all exhibit a base peak corresponding to $(M-Cl)^+$ in the CI mass spectra.

The effect of exchanging the fluorine atoms around the imine group by chlorine should result in a shift of the $C=N$ stretching frequency, which usually occurs in the region of 1780 cm^{-1} for the unreacted imines, to a much lower wavenumber. This is observed and each new imine shows a strong $C=N$ absorption near 1690 cm^{-1} in the infrared spectra.

Dehalogenation of $R_xCCl_2N=CClCFXBr:R_xCCl=NCCl_2CFXBr$

The conversion of the $-CF=NCF_2^-$ group to $-CCl=NCCl_2^-$ provides a series of highly halogenated azaalkenes that should readily undergo dehalogenation to afford hetero-dienes. Although there are a variety of methods one could use to accomplish this [8], zinc dust in sulfolane proved very effective. Sulfolane proved to be an excellent solvent since not only was it unreactive towards the imines, but its high boiling and low volatility meant that the products could easily be separated from the reaction mixture by vacuum line fractionation. The products isolated were all identified as those listed in Table 2.

It is interesting to note that in all cases elimination of BrCl occurs in such a manner that only 1,3-dienes are formed [eqn. (5)]:

$$R_xCCl_2N=CClCFXBr$$
$$R_xCCl=NCCl_2CFXBr \quad \xrightarrow[\text{Sulfolane}]{Zn} \quad R_xCCl=NCCl=CFX \qquad (5)$$

$R_x = CF_3$, C_2F_5, $ClCF_2$, $X = F$, CF_3

In order for this to occur each of the isomers must undergo dehalogenation via slightly different routes. The isomer $R_xCCl_2N=CClCFXBr$ dehalogenates by a 1,4-elimination of BrCl. The first step in this metal-induced process is probably nucleophilic attack by the zinc on the electrophilic bromine. Loss of $ZnBr^+$ results in the formation of a short-lived carbonionic intermediate [9, 10], which very rapidly, via the shift of the imine $(C=N)$ bond, eliminates Cl^- from the 4-position (Scheme 3).

The other isomer, $R_xCCl=NCCl_2CFXBr$, undergoes a 1,2-elimination of BrCl from the N-alkyl side-chain where the imine group plays no part in the elimination process. There is also the possibility that the isomer R_x-$CCl_2N=CClCFXBr$ can undergo a 1,2-elimination to form a 1,2-diene (ketenimine) of the type $R_xCCl_2N=C=CFX$. However, no such products were observed in any of the dehalogenation reactions.

All the new dienes were identified by interpreting the data given in the experimental section. Molecular ions MH^+ or M^+ were observed for each

TABLE 2

Dehalogenation of $R_xCCl_2N=CClCFXBr:R_xCCl=NCCl_2CFXBr$

Azaalkene	Conditions	Products (% yield)
$CF_3CCl_2N=CClCF_2Br$ $CF_3CCl=NCCl_2CF_2Br$	Zn/sulfolane 22 °C, 1 h	$CF_3CCl=N$, $C=C$, F, Cl, F (76)
$C_2F_5CCl_2N=CClCF_2Br$ $C_2F_5CCl=NCCl_2CF_2Br$	Zn/sulfolane 22 °C, 1 h	$C_2F_5CCl=N$, $C=C$, F, Cl, F (70)
$ClCF_2CCl_2N=CClCF_2Br$ $ClCF_2CCl=NCCl_2CF_2Br$	Zn/sulfolane 22 °C, 1 h	$ClCF_2CCl=N$, $C=C$, F, Cl, F (83)
$CF_3CCl_2N=CClCFBrCF_3$	Zn/sulfolane 22 °C, 30 min	$CF_3CCl=N$, $C=C$, F, E, Cl, CF_3 $CF_3CCl=N$ +, $C=C$, CF_3, Z, Cl, F (73) ratio E : Z ~ 1 : 9

$RxCCl_2N=CClCFX-Br$

$\downarrow$ Zn

$R_xCCl-N=CCl-CFX$ $ZnBr^+$

$\downarrow$ Cl

$R_xCCl=NCCl=CFX$ +ZnBrCl

Scheme 3.

compound in either the CI or EI mass spectra and all exhibited a strong absorption at ~ 1705 cm^{-1} [$\nu(C=N)$] and a weak absorption at ~ 1668 cm^{-1} [$\nu(C=C)$] in the infrared.

The ^{19}F NMR spectra were straightforward, those containing the $-C=CF_2$ moiety exhibiting a classic AB pattern where J_{AB} '22 Hz and $\Delta\delta_{AB} \sim 790$ Hz. In all of these examples only one isomer was observed, the stereochemistry

of which could not be determined from the data available. For the diene $CF_3CCl=NCCl=CFCF_3$, a mixture of E and Z isomers was detected, with the Z isomer being the major one formed [eqn. (5)]:

ratio $E:Z \sim 1:9$.

Conclusion

To summarize, the reaction between α,α,α'-trifluoro-perhaloazaalkenes with $AlCl_3$ provides a facile route to the formation of the corresponding α,α,α'-trichloro analogs. The practical use of the trichloro derivatives to prepare a variety of highly halogenated hetero-1,3-dienes in good yields has also been demonstrated. Further studies of the reaction chemistry of these dienes and other related compounds are currently in progress.

Acknowledgment

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AN IMPROVED SYNTHESIS OF DICHLOROFLUORAMINE, FNCl$_2$*

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SUMMARY

Low-temperature fluorination of N,N-dichloro-1-fluoroformamide, FC(O)NCl$_2$, has provided a more convenient, high-yield (75%) synthesis of dichlorofluoramine, FNCl$_2$, than was previously available. In an attempt to further expand the novel metal fluoride promoted conversion of N-Cl bonds to N-Br bonds, both FC(O)NCl$_2$ and FNCl$_2$ were reacted with bromine in the presence of various alkali metal fluorides. No evidence was found for the formation of either FC(O)NBrCl and FC(O)NBr$_2$ or FNBrCl and FNBr$_2$ in these reactions. In fact, FC(O)NCl$_2$ was found to decompose to C(O)F$_2$, N$_2$, and Cl$_2$ in the presence of alkal metal fluorides.

INTRODUCTION

In 1984 Zheng et al. reported a novel fluoride promoted conversion of N-Cl bonds to N-Br bonds as shown in eqn. (1) [1]. It then became of interest

$$CF_3NCl_2 \xrightarrow{\text{CsF/Br}_2} CF_3NBrCl \xrightarrow{\text{CsF/Br}_2} CF_3NBr_2 \qquad (1)$$

to see whether or not this methodology could be extended to the preparation of unknown N-halo amines such as FNBrCl and FNBr$_2$. However, before this investigation could be carried out, it was deemed necessary to find a more convenient and safer method of preparing laboratory quantities of dichlorofluoramine, FNCl$_2$. The results of this investigation are reported herein.

EXPERIMENTAL

The compound $FC(O)NCl_2$ was prepared by literature methods [2]. Cesium fluoride (99.9%) was activated by fusing in a Pt dish, followed by grinding in jar mill to a very fine powder under anhydrous conditions, while NaF was taken from laboratory stock and dried *in vacuo*. Bromine was dried over P_2O_5 and distilled prior to use.

Caution! *Many N-halo compounds are known to be powerful explosives; therefore, suitable safety precautions should be kept in mind. We advise that the preparations and reactions of these materials be done on a small scale.*

Infrared spectra were obtained on a Perkin-Elmer 1430 Data System; a 10-cm glass cell fitted with KCl windows was employed. Mass spectra were taken on a HP 5895A GC-MS system. ^{19}F NMR spectra were recorded on a JEOL FX-90 Q spectrometer at 84.25 MHz and referenced to internal CCl_3F.

Synthesis of dichlorofluoramine, $FNCl_2$

The dichloroamide $FC(O)NCl_2$ (3.0 mmol) was condensed into the bottom of a 150 mL stainless steel cylinder chilled to liquid-nitrogen temperature. The level of the liquid nitrogen was then raised and a slight excess of elemental fluorine (3.5 mmol) was slowly added. The reaction vessel was placed in a Dewar of evaporating liquid nitrogen and allowed to warm slowly to room temperature overnight. The vessel was then rechilled to $-196^\circ C$ and attached to the vacuum line where any noncondensible materials were removed through a scrubber filled with soda lime. The condensible materials were then transferred to the vacuum system and passed through a series of traps at -80, -115 to -120, and $-196^\circ C$. The trap at $-80^\circ C$ stopped 0.1 mmol of unreacted $FC(O)NCl_2$, while the trap maintained at between -115 and $-120^\circ C$ held the desired product $FNCl_2$ (2.25 mmol) in 75% yield. The identity and purity of the $FNCl_2$ was ascertained primarily through infrared spectroscopy [3]. The $-196^\circ C$ trap contained (3.5 mmol) primarily COF_2.

Reactions of $FC(O)NCl_2$ and $FNCl_2$ with Br_2 and/or MF, where M = Na, Cs

In a typical reaction (see Table 1), NaF (0.1 g; 2.38 mmol) was loaded into a 250-mL glass vessel in a drybox under nitrogen atmosphere. The vessel was then evacuated, and $FC(O)NCl_2$ (0.5 mmol) was condensed in at $-196^\circ C$. The reaction

TABLE 1

Reactions of FC(O)NCl$_2$ and FNCl$_2$ with Br$_2$ and/or MF, where M = Na, Cs

Reactants (mmol)		Conditions ($^{\circ}$C/h)	Volatile Products (mmol)
FC(O)NCl$_2$ (0.5)	Br$_2$ (2.0)	-196°C to RT/2-3 h RT/12 h	No Reaction
FC(O)NCl$_2$ (4.8)	CsF (10.0)	-196°C to RT/2-3 h RT/12 h	IR - COF$_2$ noncondensibles - N$_2$
FC(O)NCl$_2$ (0.5)	NaF (2.38)	-196°C to RT/2-3 h RT/12 h	COF$_2$ (0.5), Cl$_2$(0.25) noncondensibles - N$_2$
FC(O)NCl$_2$ (5.0)	NaF (15.0)/ Br$_2$ (10.0)	-196°C to RT/2-3 h RT/ 12 h	IR - COF$_2$ noncondensibles - N$_2$ unreacted Br$_2$
FC(O)NCl$_2$ (4.8)	CsF (10.0)/ Br$_2$ (10.0)	-196°C to RT/2-3 h RT/12 h	IR - COF$_2$ noncondensibles - N$_2$ unreacted Br$_2$
FNCl$_2$ (2.0)	CsF (5.0)/ Br$_2$ (5.0)	-196°C to RT/2-3 h RT/12 h	IR - FNO$_2$ (trace) [8] IR - t-N$_2$F$_2$ (trace) [9] noncondensibles- N$_2$ unreacted Br$_2$ & BrCl
FNCl$_2$ (2.25)	CsF (5.0)/ Br$_2$ (5.0)	-196°C to -50°C/2-3 h -40°C/3 h & -30°C/12 h 0°C/12 h 10°C/12 h	unreacted FNCl$_2$ (1.16) noncondensibles (0.55) unreacted Br$_2$ & BrCl

mixture was allowed to warm slowly to room temperature and react overnight. The volatile products were then moved to the vacuum line for trap-to-trap distillation. Lots of noncondensibles, presumably nitrogen, were removed during this process. The remaining condensibles, which were yellow in color, were then transferred to a trap containing mercury in order to test for the presence of chlorine. Approximately, one-third or 0.25 mmol of the condensibles were scrubbed by the mercury, and the remaining condensibles (~0.5 mmol) were shown by infrared spectroscopy to be predominantly COF_2.

RESULTS AND DISCUSSION

The need for an improved synthesis of $FNCl_2$ was recently made obvious in a report to this Journal by Gibert and co-workers [4]. In this paper, the authors overview the previous routes to $FNCl_2$ and describe their modifications to a route originally reported by Pankratov and Sokolov [5], namely the fluorination of NH_4Cl. Although this method avoids the dangers associated with preparing $FNCl_2$ from NaN_3 and ClF [6] (explosive intermediate ClN_3 [7]), it still suffers from both relatively low yields and difficulties in the separation of $FNCl_2$ from other side products such as $ClNF_2$ and Cl_2 [4]. In our investigation, we found that laboratory quantities of $ClNF_2$ could be produced in 75% yield from the low-temperature fluorination of $FC(O)NCl_2$ (eq 2). In addition, the product is easily separated from any unreacted starting

$$FC(O)NCl_2 + F_2 \xrightarrow{\text{-196}^{\circ}\text{C to RT}} FNCl_2 + COF_2 \qquad (2)$$

materials as well as the COF_2 and any other by-products formed.

The reactivity of $FC(O)NCl_2$ in the presence of bromine and alkali metal fluorides both separately and together was then studied in an attempt to prepare $FC(O)NBrCl$ and/or $FC(O)NBr_2$. The formation of either of these new haloamines was precluded by the more ready decomposition of $FC(O)NCl_2$ in the presence of fluoride ion as shown in equation 3. This observation is not surprising in view of the

$$FC(O)NCl_2 + MF \xrightarrow{\text{-196}^{\circ}\text{C to RT}} COF_2 + MCl + \tfrac{1}{2} N_2 + \tfrac{1}{2} Cl_2 \qquad (3)$$

fact that the decomposition of $FC(O)NSF_2$ to COF_2 and NSF is known to take place at temperatures as low as $0^{\circ}C$ in the presence of cesium fluoride [10]. The reaction

of $FNCl_2$ with Br_2 and CsF failed to produce any evidence for either FNBrCl or $FNBr_2$ under conditions tried (see Table 1). Again, large amounts of noncondensible gas were formed during each reaction.

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Synthesis of Novel Perhalo 1,3-Heterodienes from
N-Bromoperhalo-1-alkanimines

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The hydrolysis of several perhalo-1-bromo-3-aza-3-alkenes ($R_xCF=NCF_2CF_2Br$, $R_x = CF_3$, C_2F_5, $ClCF_2$) affords the corresponding acid amide ($R_xCONHCF_2CF_2Br$) in excellent yield. Dehydrofluorination of the amides using active KF gives the novel 1,3-heterodienes, perhalo-1-bromo-3-aza-4-oxo-2-alkenes ($R_xCON=CFCF_2Br$), in high yield. Details on the synthesis and properties of the new compounds are given along with some reaction chemistry of the dienes.

Introduction

Recently, we have reported that highly halogenated N-bromo-1-alkanimines ($R_xCF=NBr$) can be prepared in excellent yields by treatment of the corresponding perhalogenated nitrile with bromine and activated cesium fluoride.[1]

$$R_xC\equiv N + CsF + 2Br_2 \longrightarrow \underset{F}{\overset{R_x}{}}C=N\underset{Br}{} + CsBr_3$$

This one-step general synthesis combined with the good thermal stability of the imines has allowed us to investigate the chemistry of these compounds in some detail.

Previous studies of other N-halo compounds have shown that the N–X (X = Cl, Br) bond is very labile, and as a result, such compounds react quite readily under mild, thermal conditions with halogenated olefins to give 1,2-addition products.[2-6] In direct comparison, the compounds $R_xCF=NBr$ also undergo similar addition reactions with olefins to form perhalo-1-bromo-3-aza-3-alkenes ($R_xCF=NCYY'CZZ'Br$).[6] As part of this work, we have prepared a series of these addition products by treating various N-bromoperhalo-1-alkanimines with tetrafluoroethylene.

$$\underset{F}{\overset{R_x}{}}C=N\underset{Br}{} + CF_2=CF_2 \xrightarrow[24 \text{ hr.}]{140°C} \underset{F}{\overset{R_x}{}}C=N\underset{CF_2CF_2Br}{}$$

$R_x = CF_3, C_2F_5, ClCF_2$

The above compounds were typically prepared as indicated by heating the $R_xCF=NBr$ (5 mmol) and a 2-fold excess of $CF_2=CF_2$ in a Pyrex vessel. The products were easily separated from excess olefin and any unreacted N-bromo imine by vacuum-line fractionation. Although there exists the possibility of syn and anti isomerism about the C=N bond, previous NMR studies indicate that only one isomer is formed, and it is assumed on steric grounds that the observed isomer is, in each case, the one with both perhaloalkyl groups anti to each other.[6]

Further investigation of the reaction chemistry of the perhalo-N-alkyl-1-alkanimines, in particular their use as precursors to a series of highly halogenated 1,3-heterodienes, has been carried out, and the results of some of these studies are discussed herein.

Results and Discussion

Hydrolysis of $R_xCF=NCF_2CF_2Br$. Previous studies of other perhaloalkanimines have shown that they usually undergo complete or partial decomposition with H_2O at 20 °C. For example, $CF_3N=CF_2$ decomposes to give CO_2, NH_4F, and HF,[7] whereas $C_3F_7N=CF_2$ is converted to C_2F_5CN and $C_2F_5CONH_2$. With less than stoichiometric amounts of H_2O, hydrolysis is incomplete and a low yield of the corresponding isocyanate is formed.[8]

Hydrolysis of the perhalo-1-bromo-3-aza-3-alkenes in our study was carried out by shaking with an equimolar amount of H_2O at room temperature for 2–4 h. The products formed were all low-melting, white crystalline solids and were easily identified by both infrared and NMR spectroscopy as the corresponding acid amides (eq 1). The full characterization of these compounds is given

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in the Experimental Section. Conceptually the formation

$$R_x \,\diagdown \atop F \diagup C = N \diagdown CF_2CF_2Br \xrightarrow[22°C]{H_2O} R_xC(O)NCF_2CF_2Br + HF \quad (1)$$

$$R_x = CF_3, C_2F_5, ClCF_2 \qquad 65 - 70\%$$

of the amides is straightforward. Addition of H_2O to the C=N bond followed by elimination of HF gives rise to the observed products (eq 2). Due to the presence of the

$$R_x \,\diagdown \atop F \diagup C = N \diagdown CF_2CF_2Br \xrightarrow{H_2O} \left[R_x - \underset{OH}{\overset{F\ H}{C}} - NCF_2CF_2Br \right] \xrightarrow{-HF}$$

$$R_x \underset{O}{\overset{H}{C}} NCF_2CF_2Br \quad (2)$$

perhalo (R_x) group, the amides formed are quite stable and further decomposition to form isocyanates is not observed. However, long reaction times or the addition of excess H_2O does result in a decrease in the overall yield of the amide. The lower yield is caused by the amide undergoing further hydrolysis and decomposing to form other carboxylic derivatives (eq 3).

$$R_x \underset{O}{\overset{H}{C}}NCF_2CF_2Br \xrightarrow{H_2O} R_xCO_2H + BrCF_2CNH_2 \quad (3)$$

$$R_x = CF_3, C_2F_5, ClCF_2$$

While only three examples are presented here, the hydrolysis is clearly a general reaction that can be applied to the synthesis of a wide variety of amides. A large number of precursor imines are available by the addition of $R_xCF=NBr$ to almost any desired olefin.[6]

Dehydrofluorination of $R_xC(O)NHCF_2CF_2Br$. Dehydrofluorination of the amides to form perhalo-1-bromo-3-aza-4-oxo-2-alkenes (eq 4) was readily achieved by gently heating the $R_xCONHCF_2CF_2Br$ with an excess of active KF. After purification the products were isolated in ~50-60% yield. Various attempts to improve the yield

$$R_x \underset{O}{\overset{H}{C}}NCF_2CF_2Br \xrightarrow[60°C, 1\ hr.]{KF} R_xCN=C \diagup\diagdown_{CF_2Br}^{F} \quad (4)$$

were unsuccessful, and too high a reaction temperature or prolonged exposure to the KF only resulted in the formation of the decomposition products, R_xCOF and BrCF$_2$CN. Formation of these products can occur via two possible mechanisms. First of all, apart from dehydrofluorination to form the 1,3-heterodiene, the amide can undergo nucleophilic attack by F⁻ at the carbonyl center, where the elimination of BrCF$_2$CF$_2$NH⁻ accounts for the formation of R_xCOF. The nitrogen anion can then lose F⁻ to give the N(H) imine, which subsequently eliminates HF to give bromodifluoroacetonitrile (Scheme I).

Alternatively, once the N-acylimine has been formed, fluoride ion can now attack at its carbonyl center. Decomposition of the anion then formed can give rise to the observed products (Scheme II). Further experiments have shown that when the pure 1,3-heterodienes are treated with fresh KF or CsF, decomposition to the acyl fluoride and nitrile occurs quite readily, thus giving support to the

Scheme I

$$R_x\underset{O}{\overset{O}{C}}NCF_2CF_2Br \xrightarrow{F^-} R_x\underset{O^-}{\overset{F\ H}{C}}-NCF_2CF_2Br$$

$$R_x\underset{O^-}{\overset{F\ H}{C}}-NCF_2CF_2Br \longrightarrow R_xCOF + HNCF_2CF_2Br$$

$$HNCF_2CF_2Br \xrightarrow{-F^-} H-N=CFCF_2Br \xrightarrow{-HF} N\equiv CCF_2Br$$

Scheme II

$$R_x\underset{O}{\overset{O}{C}}N=C\diagup\diagdown_{F}^{CF_2Br} \xrightarrow{F^-} R_x\underset{O^-}{\overset{F}{C}}-N=C\diagup\diagdown_{F}^{CF_2Br}$$

$$R_x\underset{O^-}{\overset{F}{C}}-N=C\diagup\diagdown_{F}^{CF_2Br} \xrightarrow{-F^-} R_xCOF + BrCF_2CN$$

second mechanism. However, the first mechanism cannot be excluded on the basis of these results, and it is most likely that, during the formation of the N-acylimines, the decomposition products occur via both routes. These results also imply that, of the two reactive sites in these dienes (C=O, C=N), it is the carbonyl group that is the site of addition, which leads readily to subsequent cleavage.

It is noteworthy that these results provide additional examples of the instability of perhalogenated esters and their nitrogen analogues toward fluoride ion. It was first noted by Shreeve and co-workers that esters of the type $R_fCO_2CF(CF_3)_2$ were unstable in the presence of fluoride ion.[9] Subsequently it was shown that probably all halogenated esters of the type R_xCO_2R, where R contains an α-fluorine, are unstable to fluoride ion.[10] Later it was found that the nitrogen derivatives $R_xC(O)NFR$, containing an α-fluorine in the carboamide group, were similarly unstable.[11] With the current results, the generality of this reaction type is extended to N-chloroperhaloalkanamides (see later discussion). These three reaction types are shown in eqs 5–7 (R = halo or perhaloalkyl containing an α-fluorine on the carbon bound to O and N, R′ = alkyl, halo, or perhaloalkyl, and R_x = halo or perhaloalkyl.)

$$R_x\underset{O}{\overset{O}{C}}-OR \xrightarrow{F^-} R_x\overset{O}{C}F + R'\overset{O}{C}F \quad (5)$$

$$R_x\underset{O}{\overset{X}{C}}-NR \xrightarrow{F^-} R_x\overset{O}{C}-F + R'CF=N-X \quad (6)$$

$$(X=F, Cl)$$

$$R_x\underset{O}{\overset{O}{C}}-N=CFR' \xrightarrow{F^-} R_x\underset{O}{\overset{O}{C}}-F + R'C\equiv N \quad (7)$$

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Scheme III

In eq 6, if R = CF$_3$ and X = F, the compounds do not undergo the indicated reaction,[12] and if X = Cl, a similar limitation when R = CF$_3$ is likely. However, routes to the latter compounds are not presently available. For eq 5 we predict a similar stability for X = F and R = CF$_3$, but the only example of this type, CF$_3$C(O)OCF$_3$,[13] is difficult to prepare, and its reaction with fluoride has not been carried out.

The identity of the new perhalo *N*-acylimines is strongly supported by the data given in the Experimental Section. Molecular ions MH$^+$ are observed for each compound in the chemical-ionization (CI) mass spectra, and each contains two strong absorptions in the infrared at ~1795 and 1765 cm^{-1} due to ν(C=O) and ν(C=N), respectively. In all cases for the N=CF^{B}CF$_2$^{C}Br moiety, the ^{19}F NMR spectrum exhibits a doublet near δ -62 for the fluorines labeled C and a broad triplet near δ -34 for the vinylic fluorine B. The coupling constant J_{BC} has a value of 10-11 Hz. No long-range ^5J or ^6J F–F coupling was observed as has been reported for CF$_3$C(O)N=C(CF$_3$)$_2$.[14]

Reaction of CF$_3$C(O)N=CFCF$_2$Br with ClF. In this paper we only touch on the reaction chemistry of these dienes. A major interest to us was the polar addition of ClF across the C=N bond and whether or not the reaction would lead readily to C—N bond cleavage, forming NCl$_2$ derivatives.[14] The addition of ClF yields the corresponding *N*-chloroalkanamide in almost quantitative yield (eq 8).

$$CF_3\underset{O}{\overset{Cl}{C}}N = CFCF_2Br + ClF \longrightarrow CF_3\underset{O}{\overset{Cl}{C}} - N - CF_2CF_2Br \qquad (8)$$

The completion of the reaction was readily ascertained due to the disappearance of the C=N stretching frequency at 1764 cm^{-1}, coupled with a shift of the C=O stretching frequency from 1793 to 1772 cm^{-1} in the infrared spectrum. For CF$_3$C(O)N(Cl)CF$_2$CF$_2$Br, in the ^{19}F NMR spectrum, long-range spin–spin coupling between the acyl CF$_3$ and NCF$_2$ groups is observed (^5J = 3.9 Hz).

When the above reaction was carried out with a slight excess of ClF, CF$_3$C(O)N(Cl)CF$_2$CF$_2$Br was still the major product formed; however, small amounts of CF$_3$COF and BrCF$_2$CF$_2$NCl$_2$ were detected. These two products are probably formed by the further reaction of ClF with the N—C=O bond.[14]

The *N*-chloroalkanamide is thermally very stable. However, as previously mentioned, it has been shown to be unstable in the presence of fluoride ion. In the presence of CsF, CF$_3$C(O)N(Cl)CF$_2$CF$_2$Br decomposes very rapidly to form CF$_3$COF and BrCF$_2$CF=NCl. The probable mechanism of this decomposition is outlined in Scheme III.

The ^{19}F NMR spectrum for BrCF$_2$^{A}CF^B=NCl shows two peaks at δ -57.9 (d) and δ -40.6 (t) which are due to the fluorines labeled A and B, respectively. In all of the NBr and NCl imines we have previously prepared,[1,15] the vinylic fluorine usually appears in the region of δ -20 to -30 (upfield from CFCl$_3$), which we attribute to the compounds adopting the syn configuration. The shift of B to a higher field suggests that the *N*-chloroimine formed in the decomposition reaction adopts the anti configuration as indicated in Scheme III.

Conclusion

The practical use of perhaloazaalkenes to prepare a variety of secondary amides in good yield, by hydrolysis with H$_2$O, has been demonstrated. These compounds easily undergo dehydrofluorination using KF to afford a novel class of perhalo 1,3-heterodienes. Further studies of the reactions of these new dienes are in progress.

Experimental Section

General Procedure for the Hydrolysis of R$_x$CF=NCF$_2$CF$_2$Br. R$_x$CF=NCF$_2$CF$_2$Br (5.0 mmol) and H$_2$O (5.0 mmol) were both condensed into a 50-mL Pyrex flask fitted with a glass–Teflon stopcock. The vessel was then warmed and shaken at room temperature for 2–4 h. Trap-to-trap fractionation (-10, -96, and -196 °C) afforded the corresponding amide in the -10 °C trap, and any unreacted R$_x$CF=NCF$_2$CF$_2$Br was collected in the -96 °C trap. Yields were typically 65–70%, and the compounds were characterized as follows.

CF$_3$C(O)NHCF$_2$CF$_2$Br: mp 29.5 °C; IR (gas) 3554 (w), 3460 (vs, NH), 1799 (vs, C=O), 1656 (w), 1523 (vs), 1354 (w), 1328 (w), 1260 (s), 1232 (vs), 1184 (vs), 1129 (vs), 1099 (vs), 1029 (w), 935 (vs), 792 (m), 771 (m), 723 (s), 702 (s), 645 (s), 626 (m) cm^{-1}; MS (CI, major) m/z 294/292 [(M + 1)$^+$, 100], 274/272 [(M – F)$^+$], 224/222 [(M – CF$_3$)$^+$], 212 [(M – Br)$^+$], 181/179 (C$_2$F$_4$Br$^+$), 131/129 (CF$_2$Br$^+$), (EI, major) 274/272 [(M – F)$^+$], 212 [(M – Br)$^+$], 196/194 [(M – CF$_3$CO)$^+$], 162 [(M – CF$_2$Br)$^+$, 100] 131/239 (CF$_2$Br$^+$), 119 (C$_2$F$_5$$^+$), 100 (C$_2F_4$$^+$), 69 (CF$_3$$^+$); ^{19}F NMR, CF$_3$^{A}C(O)NHCF$_2^{B}CF_2$^{C}Br (d$_6$-acetone) δ_A -75.6, δ_B -94.2 (q), δ_C -67.2 (t), J_{BC} = 4.5, J_{HF} = 4.5 Hz; ^{1}H NMR δ 10.85 (br).

CF$_3$CF$_2$C(O)NHCF$_2$CF$_2$Br: mp 36 °C; IR (gas) 3555 (w), 3458 (s, NH), 1790 (vs, C=O), 1520 (vs), 1340 (s), 1290 (s), 1221 (vs), 1179 (s), 1135 (m), 1101 (vs), 1031 (vs), 931 (vs), 868 (w), 720 (w), 703 (m) cm^{-1}; MS (CI, major) m/z 344/342 [(M + 1)$^+$, 100], 324/322 [(M – F)$^+$], 276/274 [(M – CF$_3$)$^+$], 262 [(M – Br)$^+$], 181/179 (C$_2$F$_4$Br$^+$), (EI, major) 276/274 [(M – CF$_3$)$^+$], 224/222

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